Catalytic Dehydrogenation Properties of Supported Carbon

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Introduction

The catalytic dehydrogenation of hydrocarbons such as higher normal paraffins and of low molecular weight paraffins is usually associated with supported metals (e.g. platinum) or with supported metal oxides (e.g. chromia, molybdena). The thermodynamics of dehydrogenation generally require relatively high reaction temperatures (above 400°C) to achieve commercially useful levels of conversion. At these high temperatures there is a tendency for supported metal and metal oxide catalysts to "coke" (accumulate carbonaceous deposits) and experience an accompanying decay in catalyst activity. Thus "coking" of supported catalysts and catalyst deactivation are almost synonymous. We were, therefore, quite surprised to discover (1,2) that supported carbon, e.g. carbon on activated alumina, possesses interesting catalytic dehydrogenation properties of a fairly general nature and can be used to dehydrogenate paraffins, olefins and alkyl-substituted aromatics.

Catalyst Preparation

Supported carbon catalysts can be produced in various ways but are perhaps most conveniently prepared by the pyrolysis of a wide variety of hydrocarbons on the surface of porous supports such as activated alumina. The pyrolysis can be conducted in a fixed bed reactor containing the support particles, preferably at a temperature in excess of 500°C. Preferably the hydrocarbon used to generate the deposited carbon is an unsaturated molecule since unsaturated species tend to exhibit higher rates of carbonization. Suitable carbonizing molecules include styrene, vinylic monomers, low molecular weight olefins, etc. Carbon loadings in the vicinity of 8-10 wt % carbon were found to be useful.

It has been found that the acidity of the alumina support has a profound effect on the state of dispersion of supported carbon and that ESR measurements can be used to determine the state of dispersion (3). Low acidity is conducive to obtaining a high degree of dispersion of the the carbon phase whereas high acidity tends to produce carbon clusters. Techniques for measuring the acidity of supports using model reactions have been described (1,2). Low acidity can be readily imparted to an activated alumina support by the addition of small amounts of alkali metal, such as 0.3 - 2.0% sodium. While catalytic dehydrogenation can also be observed with activated carbon free of associated metal oxide support, the selectivity for catalytic dehydrogenation is observed to be lower. This is ascribed to the fine pore structure of activated carbons.

Ethylbenzene Dehydrogenation Results

The dehydrogenation of ethylbenzene is illustrated by the following results. 1/8 inch tablets of gamma alumina were treated by the addition of 2 wt % Na derived from the impregnation of aqueous sodium nitrate followed by calcination. Carbonization was conducted using a feedstock that was about 1/3 styrene and 2/3 ethylbenzene at a temperature of 540°C with nitrogen as a diluent in a mol ratio of nitrogen to hydrocarbon of 7.5:1. The reactor pressure was substantially atmospheric pressure and the LHSV of the hydrocarbons was 0.22 hr^{-1}. The carbonization was conducted for six hours following which the synthesis of styrene from ethylbenzene was initiated using steam as a diluent. The mol ratio of steam to ethylbenzene was 7.5:1. At a reaction temperature of 540°C, with a LHSV of ethylbenzene of 0.24 hr^{-1}, the conversion to styrene is 36.5% with a selectivity of 96.5%. When the ethylbenzene LHSV was changed to 0.12 hr^{-1}, the conversion to styrene was 41% with a selectivity of 96%. It was observed that a slow but progressive state of deactivation occurs, but that the rate of deactivation is much less with steam than with nitrogen as diluent with the same catalyst and reaction conditions.

Other examples of catalytic dehydrogenation are given (1,2) for the dehydrogenation of higher normal paraffins to linear olefins, butenes to butadiene, propane to propylene.

Free Radical Catalyst Properties

ESR measurements (3) have shown that the supported carbon catalysts have an appreciable concentration of unpaired electrons in the carbon phase which is in a high state of dispersion on low acidity alumina. These unpaired electrons appear to be free radical sites. Thus the supported carbon catalyst seems to constitute a solid free radical that is capable of promoting dehydrogenation by a free radical mechanism

comprising sequential H atom abstraction reactions. When dehydrogenating 2,4,4-trimethylpentene-2 over supported carbon, one obtains a high selectivity among xylenes to para xylene. This is consistent with a free radical dehydrogenation mechanism wherein the reaction proceeds by a 1,2 vinyl shift to produce a 2,5-dimethyl-hexene-2 radical as an intermediate to para xylene.

Relation to Molybdena-alumina

The supported carbon catalyst gives results very similar to those obtained with molybdena-alumina in the dehydrogenation of n-dodecane to linear dodecenes. The similarity in activity, selectivity and deactivation is so striking that it appears that the selective dehydrogenation observed after break-in of molybdena-alumina arises not from active sites characteristic of the original fresh catalyst but rather from sites on the carbonaceous phase that has been deposited.

References

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