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The Activities of Lead Oxide-Silica Gel Catalyst for Acrylonitrile Synthesis from Propylene and Nitric Oxide

A catalytic process was patented for acrylonitrile synthesis from propylene and nitric oxide that employs lead titanate catalyst (*1*). We have reported that the activity of this kind of catalyst depends on the valence change of lead (*2*). A new type catalyst, lead oxide supported on silica gel, is investigated in this paper which showed high activity for the reaction. It seems reasonable to conclude that lead ion (II) plays a role of the active center in this catalyst from the result of correlation between the X-ray diffraction and activity for acrylonitrile formation (*2*). The effects of lead oxide concentration on the conversions of propylene and nitric oxide and on the selectivities of the products are also examined to elucidate the working state of the catalysis. The products of this reaction are acrylonitrile, acetonitrile, carbon dioxide, and higher boiling materials.

Experimental

The experiments were carried out with a conventional fixed-bed flow reactor heated in a cylindrical furnace. The purity of propylene was 99.8%, and the impurities were propane and ethane. Nitric oxide was produced by adding ferrous sulfate powder into aqueous solution of sodium nitrate (*3*). A small amount of higher oxides of nitrogen was removed by 10% aqueous sodium hydroxide solution. The purity of nitric oxide was 97% and nitrogen was detected as a sole impurity. Nitrogen was also fed to reactor as a diluent gas. The catalyst was prepared in the following way. Aqueous solution of lead nitrate was added dropwisely over a period of several hours to the rapidly stirred aqueous slurry of silica gel (60–80 mesh, having a BET surface area of 530 m^2/g) heated in an oil bath maintained at 120–130°C. The quantity of lead nitrate was dosed to give the desired concentration of lead ion in the finished catalyst. The aqueous slurry of the silica gel was subjected to heat in an oil bath for additional 3 hr followed by evaporation to dryness in an oven at 100°C, and formed into tablets of 3 mm dia. × 2 mm. Prior to use, the tablets were calcined in air at 500°C for 6 hr. The liquid products were analyzed by packed column gas chromatography (10% of di-nonyl phthalate on Chromosorb-W). Analyses of propylene and nitric oxide at the inlet and outlet of the reactor were made by gas chromatography by use of the columns packed with alumina and molecular sieve 5A, respectively. The temperature of the reaction zone was controlled within ±1°C.

Results and Discussion

Lead oxide carried on the catalyst were from 0.6 to 35.1 wt %. Lead atoms were proved to be well dispersed on the surface of silica gel by X-ray diffraction and electronic microscope as well (*2*). Fig. 1 shows the marked linear increase in catalytic activity with the increase in lead ion concen-

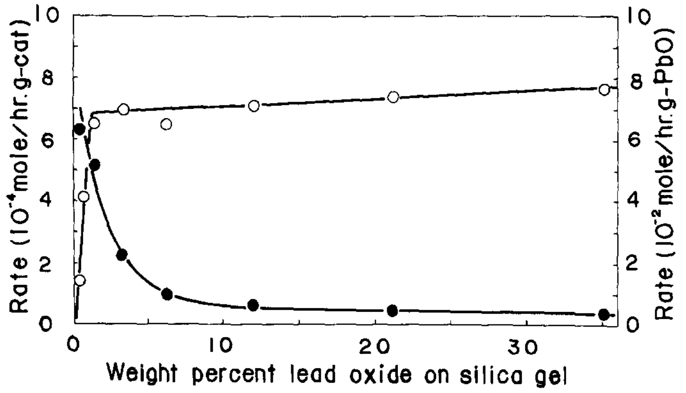

FIG. 1. Effect of lead ion concentration on rate of acrylonitrile formation. The data were obtained at 500°C and at propylene, nitric oxide and nitrogen partial pressures of 0.18, 0.27, and 0.55 atm., respectively. ○: Rate of acrylonitrile formation per unit weight of catalyst. ●: Rate of acrylonitrile formation per unit weight of lead oxide (II) on silica gel.

tration up to about 1.5 wt %, where the rate of acrylonitrile formation amounted to 7.0×10^{-4} mole/hr. g-catalyst. Further increase in lead ion concentration resulted in the little increase in yield of acrylonitrile, where the conversions of propylene and nitric oxide were 45% and 75%, respectively. The linear relationship between catalyst activity and lead ion content below 1.5 wt % concentration of the latter means that each increment of the lead ion is equally effective until the optimum concentration is reached. Thus, a series of catalysts were divided into two classes, that is, the catalyst with the lower content of lead ion, and with the higher one. The different behaviors of these two catalysts mentioned below should be ascribed to the difference in the rate determining step.

Activation energies were measured by the catalysts of each classes; based on which the reaction mechanisms were discussed. The experiments were carried out by use of 1.33 wt % (0.361 mole %) and 21.2 wt % (6.74 mole %) of lead ion as each typical example of catalyst, respectively, at four temperature levels between 460 and 520°C. The initial rates of acrylonitrile formation per unit weight of catalyst (r_0) were measured. As shown in Fig. 2, activation energy was 44 kcal/mole for the catalyst containing 1.33 wt % of lead oxide, whereas it was 2 kcal/mole for the catalyst containing 21.2 wt % of lead oxide.

Since the activation energy of 44 kcal/mole was observed in the region in which the rate of acrylonitrile formation is proportional to the concentration of lead ion supported on silica gel, the chemical reaction on the surface of the catalyst is considered to be the rate determining step. On the other hand, in the case of the latter catalyst with small activation energy, physical process will control the overall reaction rate, and the rate of chemical reaction on the catalyst surface is in equilibrium with that of physical process. If the chemical reaction is so fast and the rate of reactant consumption depends on diffusion,

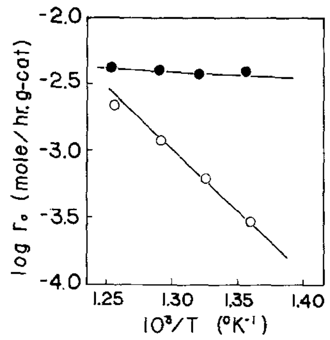

FIG. 2. Arrhenius plots for acrylonitrile formation over silica-supported lead oxide. The data were obtained at propylene, nitric oxide and nitrogen partial pressure of 0.18, 0.27, and 0.55 atm, respectively. ○: PbO/SiO$_2$ = 1.33 wt % E_{act} = 44 kcal/mole ●: PbO/SiO$_2$ = 21.2 wt % E_{act} = 2 kcal/mole.

then the observed activation energy will be less than the true value, but greater than one-half of its true value. Since the true activation energy is 44 kcal/mole where diffusion does not influence the rate, that is, in small pores where the rate is proportional to k, 22 kcal/mole would be expected for the minimum value of activation energy in this synthetic reaction (*4*). Consequently, the diffusion of reactants (propylene and nitric oxide) in pores did not influence the rate. Other diffusion process, for example, diffusion of gases to surface particles, or the diffusion of products in small pores can be considered to control the reaction rate. These activation energies would be about RT, namely 1.5 kcal/mole at 500°C. In fact, the value of 2 kcal/mole calculated by the method of least squares, observed in the experiments over the catalyst with high lead ion content was in good agreement with the expected value.

In the previous paper (*2*), it was reported that the polymer was formed by consecutive reaction of produced nitriles. A large amount of polymer (acrylonitrile 40%, polymer 45% on carbon basis) was formed over the catalyst with high lead ion concentration whereas it was small (acrylonitrile 78%, polymer 7%) in low content one. This phenomenon could be explained by the decreased chances of the interaction between the adsorbed molecules due to the less probability of the neighboring active sites on the surface with the lower lead content of catalyst. However, polymer yield based on total catalyst was noticed over the catalyst with 6 wt % of lead oxide content. When the catalyst with high surface concentration of lead ion was used, the surface chemical reaction is so fast that the accumulation of the adsorbed acrylonitrile on the surface increased, which enhances the reaction to form polymers. This fact might suggest that diffusion of the product would be slow compared with the other rate processes, and the rate of reaction over the catalyst with higher lead ion concentration would be controlled by the process of diffusion of the produced molecule. The proposed scheme is supported by the results on polymer formation.

It is concluded from the results of this investigation that the lead ion plays an important role as the active center for the synthetic reaction and that the increase in surface concentration of lead ion leads to the change in rate determining step.

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IR Study of Synergetic Effect on Adsorption of Carbon Monoxide on Nickel Oxide

In the previous work (*1*), synergetic effect of oxide catalysts with different dopents on catalytic activity has been reported for the carbon monoxide oxidation reaction over nickel and zinc oxide catalysts. The enhanced catalytic activity of mixtures of the same oxide but with different dopents was explained by the n-p junction model of