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 semiconductors as follows: When the same oxide but with different dopents are brought into contact, electron rearrangement will occur in such a way as to equalize Fermi levels at the interface. Electrons are transferred from the oxide with high Fermi level (e.g., In doped NiO, hereafter represented as NiO(In)) to the oxide with low level (e.g., NiO(Li)). The resulting positive and negative charges favor the chemisorption of CO and O_2 as charged species, CO^+ and O^-, respectively. The increased amount of adsorbed CO^+ and O^- was concluded to be responsible for the observed enhancement of reaction rate.

The aim of present work is to obtain experimental support for the foregoing discussion by IR study of CO adsorbed on nickel catalyst.

Both transmittance of mixtures of NiO (Li), NiO(In), and the Aerosil and adsorption amount of CO on the mixtures were so small that it was impossible to do the spectroscopic study. Therefore, homogeneous mixtures of nickel nitrate coated Aerosil after O'Neill (*2*) and NiO(5 at% Li) or NiO(2 at% In), and the coated Aerosil were pressed (1.8 t/cm^2) into discs (20 mm in dia). NiO(Li) and NiO(In) were here sintered at 600°C for 15 hr and have surface areas of 2.5 and 10.9 m^2/g, respectively. The discs were fired in vacuum for 22 hr at 400°C in an infrared cell. The resulting nickel oxide coated Aerosil was represented as NiO(p) and had surface area of 140 m^2/g. After this procedure the sample was allowed to cool down to room temperature, and the background was recorded; then the carbon monoxide of 22 Torr was introduced. The spectrum was recorded at 5 min, 2 and 20 hr after introduction of the gas. Absorption bands at 2195, 2170, 2125, and 2060 cm^{-1} appeared together with a broad band at 1800–1500 cm^{-1} for all of these samples. The absorption band at 2060 cm^{-1} assigned to the linear form of adsorbed CO on nickel (*3–5*) was strongest among the bands cited previously. Attention, therefore, has been paid exclusively to the change of transmittance at 2060 cm^{-1}. Addition of NiO(Li) and NiO (In) to NiO(p) increased and decreased the absorption at 2060 cm^{-1}, respectively, as shown in Fig. 1.

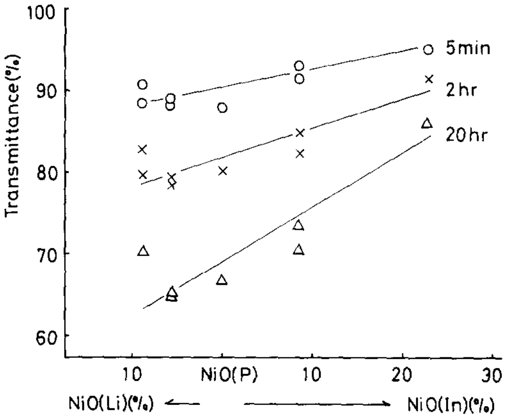

FIG. 1. Composition of samples and transmittance at 2060 cm^{-1}. Weight per cent of doped oxides added to NiO(p) is recorded on abscissa.

The result can be interpreted by considering electron rearrangement between NiO(Li) and NiO(p), and NiO(In) and NiO(p). The state of packing two mixtures may be expressed schematically as shown in Fig. 2. The total surface area of NiO(p) in the samples is so large in comparison with those of NiO(Li) and NiO(In) that the adsorption amount of CO on NiO(Li) and NiO(In) can be negligible. The increased and decreased absorption observed, therefore, are thought to be caused by a change of the adsorption amount of CO on NiO(p) due to the addition of the doped oxide. From the foregoing discussion, the positive and negative charge will be induced on NiO(p) for the mixture NiO(Li)

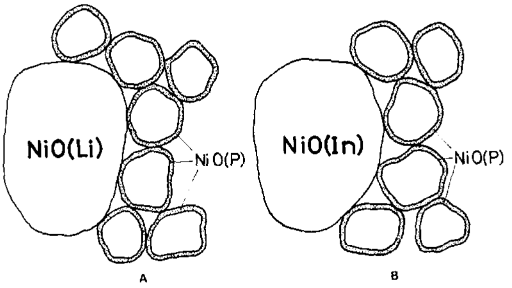

FIG. 2. Schematic models of packing state in two samples; (a) NiO(Li) and NiO(p), and (b) NiO(In) and NiO(p).

and NiO(p), and NiO(In) and NiO(p), respectively. If the positive charge on NiO (p) favors the chemisorption of CO as CO^+, the trend recorded in Fig. 1 can be elucidated.

From the result obtained, the authors concluded that the synergetic effect of oxides with different dopents also was supported by IR study of adsorbed CO on nickel oxide.

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