Complete Removal of NO by Means of a Gas–Solid Catalytic Reaction

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Summary Complete conversion of NO, irrespective of the coexistence of O_2, was achieved without additional reductive gas at < 420 °C by the use of composite catalysts supported on active carbon.

Many efforts have been concentrated recently to remove detrimental NO in exhaust gases from various internal combustion engines and furnaces by means of catalytic conversion.[1,2] The most simple method for NO removal is the direct decomposition of NO into N_2 and O_2. Some reduced metallic catalysts have high activities for NO decomposition, but are deactivated rapidly owing to the oxygen released from the decomposed NO combining with the metals. In contrast, oxide catalysts, such as perovskite, are stable against oxidative reaction conditions, but have low activities for NO decomposition.[2,3] Therefore, NO has usually been made to react with some gaseous reducing agents such as hydrogen or ammonia.[2] However, this method is troublesome to apply for small sources or moving vehicles.

We present here a novel and simple method to convert NO into innoxious gases without any additional gaseous reducing agents, at relatively low temperatures by a catalytic gas–solid reaction with a continuous flow method at atmospheric pressure.

The composite catalyst systems, which had been found to exert high activities both in methanation of carbon oxides[4] and direct hydrogenation of carbon,[5] were applied in this study. An ordinary active carbon, 30—60 mesh in size, supplied by Shimadzu Seisakusho Co. Ltd. was used as the catalyst support. It had a B.E.T. (Brunauer, Emmett, and Teller) surface area of 1230 $m^2 g^{-1}$, a porosity of 0·46 $cm^3 cm^{-3}$, a bulk density of 0·32 $g cm^{-3}$, and had two different pore-diameter distributions *i.e.*, a macropore of $\approx 3 \mu m$ and a micropore of ≈ 26 Å. A water soluble component was not detected. Volatile matter below 500 °C in a stream of nitrogen containing 10% hydrogen was negligible. Catalyst constituents were supported by impregnation of aqueous nitrate solution, followed by thermal decomposition and successive hydrogen reduction. Several weight percent of an iron-group metal was supported as the catalyst substrate on the active carbon. Small amounts of a rare-earth oxide and a platinum-group metal were combined with the substrate as promoters. The atomic ratios of both promoters were set at *ca.* 0·2 and 0·02 of the substrate, respectively. In the case of the three-component catalyst, the platinum-group metal was first dispersed on the support, and then the other two components were additionally supported simultaneously.

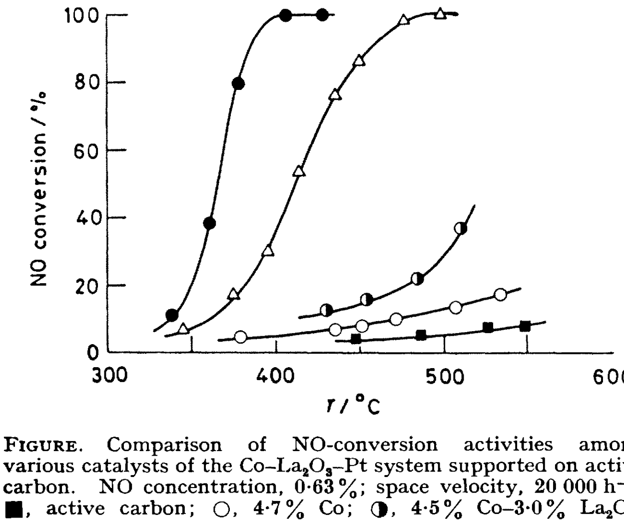

Figure. Comparison of NO-conversion activities among various catalysts of the Co–La_2O_3–Pt system supported on active carbon. NO concentration, 0·63%; space velocity, 20 000 h^{-1}; ■, active carbon; ○, 4·7% Co; ◑, 4·5% Co–3·0% La_2O_3; △, 0·7% Pt; ●, 4·6% Co–2·5% La_2O_3–0·7% Pt.

The catalysts were treated with a nitrogen stream containing 0·63% NO at a space velocity of 20 000 h^{-1}. Temperature dependences of NO conversion for various catalysts are shown in the Figure, with the catalyst system of Co–La_2O_3–Pt as an example. As can be seen in the Figure, the three-component catalyst exerted a synergistic effect. Its activity is far beyond the sum of the constituent single-component catalysts. The NO conversion occurred above 300 °C, consuming the active carbon, the complete conversion into innoxious N_2 and CO_2 being achieved at $<$ 400 °C. Toxic carbon monoxide was not detected in the effluent gas. Minor activity was exhibited by the active carbon itself under these conditions.

The conversion rate of O_2 into CO_2 by the use of the three-component catalyst was higher than that of NO. Accordingly, in spite of the coexistence of O_2 in a concentration equivalent to that of NO, *i.e.*, 0·2—2%, the NO was still completely converted below 420 °C in succession to the complete O_2-conversion. The presence of at least 2% of water vapour and carbon dioxide at reaction temperatures below 500 °C was observed to have no effect. When a reducing gas, such as hydrogen, carbon monoxide, or ammonia, was added to the inlet gas in excess of the stoicheiometry, NO could be converted completely by the catalytic surface-reaction at lower temperatures; *e.g.* $<$ 200 °C.

The space–time conversion of NO at 500 °C increased until 70% of the carbon was consumed at a constant flow rate, and attained such high values as 140 mol $kg^{-1} h^{-1}$. The active carbon was consumed almost completely when the reaction-gas flow was continued for a long enough time. Results with active carbons from a number of sources, *i.e.*, Merck-Art 2186, Nakarai Chemicals-M8N, and Nakarai Chemicals—bone charcoal showed that a greater reaction rate is obtained with the source having a relatively smaller pore-volume. It indicates that pitting of catalyst particles proceeds more smoothly in these active carbons.

The order of the activity for each catalyst constituent was as follows. For the catalyst substrate, Co $\geqslant$ Fe $\geqslant$ Ni; for both promoters, $La_2O_3 > ThO_2 \simeq Ce_2O_3$ and Pt $>$ Pd $>$ Rh $>$ Ru.

These results clearly demonstrate the synergistic effect of the composite catalysts in the gas–solid reaction, and exhibit a potential for simple application to many small scale NO sources.

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