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Catalytic decomposition of N_2O

J. Haber*, T. Machej, J. Janas, M. Nattich

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Cracow, Poland

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Abstract

Decomposition of N_2O in the temperature range 200–500 °C was studied on catalysts composed of rhodium supported on γ-Al_2O_3 doped with different amounts of Li, Na, K, Cs cations. It has been found that doping with alkali metals influences the dispersion of rhodium which is reflected in the changes of catalytic activity. Dependence of activity on dispersion is linear for potassium and cesium, whereas in the case of sodium a dramatic decrease of activity is observed when the concentration of sodium surpasses 0.07–0.08 mol% due to the modification of the number or specific activity of active sites. The detrimental effect of sodium may be compensated by doping with potassium.

Keywords: N_2O decomposition; Rhodium catalyst; Alkali metals

1. Introduction

Nitrous oxide is a dangerous environmental pollutant because it contributes to the destruction of stratospheric ozone being at the same time a greenhouse gas. The concentration of N_2O in the atmosphere continues to increase (0.2–0.3% yearly) and this increase appears to be caused mainly by anthropogenic activities [1,2]. Chemical processes associated with the production and use of nitric acid and fluidized bed combustion are the two main nitrous oxide sources, and their contribution to the total nitrous oxide emissions amounts to about 20% [3].

Reduction of N_2O emission can be achieved principally in two ways, either by lowering the formation of N_2O or after treatment where catalysis offers a route for N_2O abatement by the direct decomposition into nitrogen and oxygen.

Transition metal oxides, zeolites and noble metals, especially rhodium, dispersed on oxide supports show catalytic activity in N_2O decomposition [4–7]. Rhodium supported on γ-alumina is one of the potential commercial catalyst.

The activity of catalysts containing noble metals depends on the properties of γ-alumina used as a support. Commercial aluminas contain different amounts of sodium ions, modifying the local crystal structure on alumina surface which may have some impact on the activity of noble metals [8,9].

In an attempt to scale-up the process, commercial aluminas, containing different amount of sodium, have been used as supports for rhodium. It has been found that the catalyst performance in N_2O decomposition strongly depends on the sodium content in Al_2O_3. For high concentration of sodium (0.8 mol%) the catalyst activity was poor.

It seemed therefore of interest from both fundamental and applied research point of view to investigate the influence of the presence of alkali metal ions on the activity of catalysts in nitrous oxide decomposition.

2. Experimental

2.1. Materials

Commercial γ-Al_2O_3 (Procatalyse, Spheralite 531), containing trace amounts of Na_2O was used as a support for further studies.

Alumina was impregnated with different amounts of lithium, sodium, potassium and cesium carbonates followed by drying at 120 °C for 2 h and then calcining at 550 °C for 5 h.

Supports prepared in this way were impregnated with an aqueous solution of rhodium nitrate. The samples, after drying, were activated in reducing atmosphere at 550 °C for 1 h. The resulting catalysts contained 0.1 w/w (%) Rh and 0.033–0.099 mol% of appropriate alkali oxide.

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* Corresponding author. Tel.: +48-12-6395152; fax: +48-12-4251923.
E-mail address: nchaber@cyf-kr.edu.pl (J. Haber).

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2.2. Methods

The catalytic tests were performed in the flow reactor at GHSV = 4000 h^{-1} with nitrogen as a carrier gas. The concentration of N_2O in nitrogen was 1.0 v/v (%) and N_2O decomposition was studied in the temperature range 200–500 °C.

BET surface area was determined from nitrogen adsorption at 77 K. The specific surface area of pure γ-Al_2O_3 was 110 m^2/g. The BET surface area of the samples changed after impregnation and calcination to a small extent only and was equal to 125 m^2/g for all catalysts.

Dispersion of rhodium was determined by adsorption of hydrogen at room temperature assuming H/Rh ratio equal to 1. As the results were used for comparison of the catalysts only, the assumption of the value of H/Rh ratio could not bear upon the conclusions.

3. Results and discussion

Fig. 1 shows the light-off curves of the decomposition of N_2O for a series of samples doped with different amounts of Na_2O. It may be seen that catalytic activity strongly depends on the concentration of the dopant. In case of undoped sample the reaction starts around 300 °C and attains 100% conversion at 425 °C. Doping with small amounts of Na_2O increases the activity, so that, for the sample containing 0.078 mol% Na_2O the reaction starts at 275 °C and 100% conversion is attained at 375 °C. Further increase of the amount of dopant has a detrimental effect on the activity. Similar behaviour is observed in the case of catalysts doped with lithium. In the case of samples doped with potassium and cesium the activity at first increases with the amount of dopant and then attains a plateau.

The results of the studies of catalytic activity of samples, doped with different amounts of the four alkali metal cations are summarized in Fig. 2, in which, the activity, expressed in terms of the temperature of 50% conversion, is plotted as a function of the concentration of dopant for the whole series of alkaline metal oxides. It may be seen that a sharp maximum of catalytic activity (minimum of $T_{50\%}$) is attained at the concentration of about 0.08 mol% for lithium and sodium containing samples, whereas in the case of the potassium and cesium containing samples a plateau is attained around this concentration, corresponding to higher catalytic activity than that observed at maximum in the case of lithium and sodium.

The measurements of BET surface area, which is practically that of alumina as a support, have shown that it has similar value for all samples and is not affected by doping. A hypothesis could be thus advanced that it is the dispersion of rhodium which is influenced by introduction of alkali metals and whose modification is responsible for the observed changes of catalytic activity. Fig. 3 shows the dispersion, as determined by hydrogen adsorption, as a function of the concentration of dopant for all four alkali metals. Comparison of Fig. 3 with Fig. 2 shows that the two functions are mirror images and leads to the conclusion that the changes of catalytic activity follow in general the changes of the Rh dispersion.

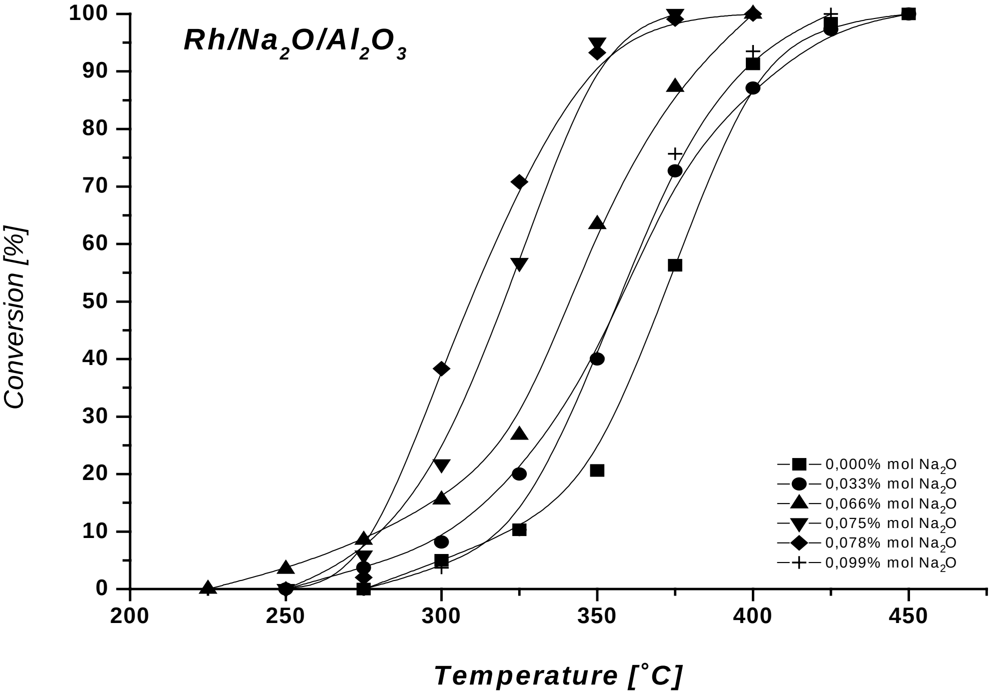

Fig. 1. Temperature dependence of N_2O conversion for $Rh/Na_2O/Al_2O_3$ catalyst samples containing different sodium contents.

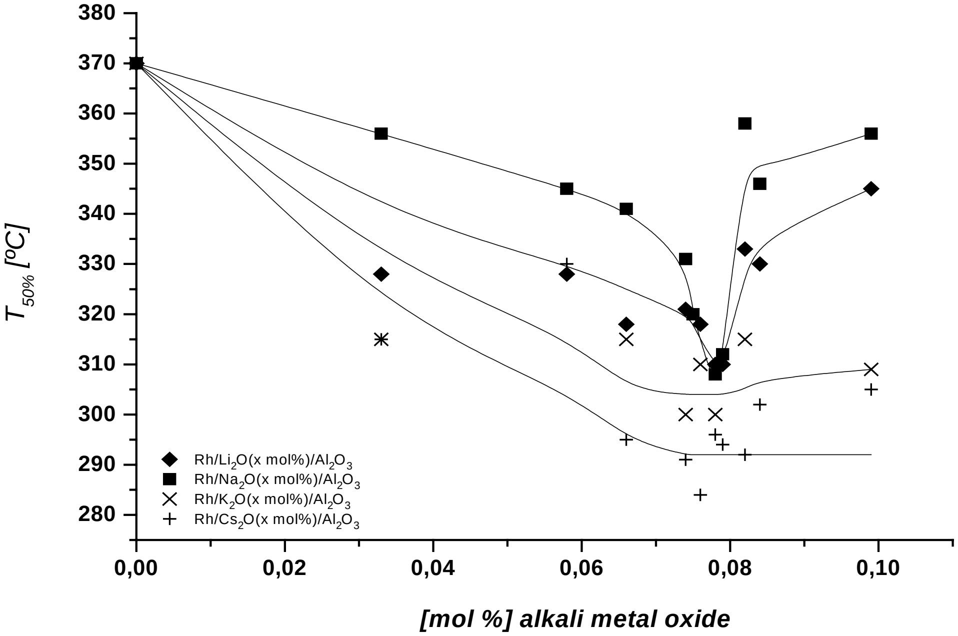

Fig. 2. Temperature of 50% N_2O conversion as a function of the amount of Li, Na, K and Cs supported on γ-Al_2O_3 for Rh/alkali metal oxide/Al_2O_3 catalysts.

In order to check whether modification of the dispersion of rhodium is the only factor influencing catalytic activity the latter was plotted as a function of the dispersion of rhodium for the series of samples doped with different amounts of Na_2O (Fig. 4). A linear dependence was obtained for samples containing small amounts of Na_2O up to the value of 0.08 mol% indicating that the change of catalytic activity is due to the modification of rhodium dispersion. The point representing behaviour of the sample containing 0.099 mol% of Na_2O lies well below the line representing the other samples which shows that some other factor must have influenced the catalytic activity. This conclusion is confirmed by the calculation of turnover frequencies (TOF). If the changes of dispersion were the only factor responsible for the variation of catalytic activity the value of TOF should be independent of the concentration of dopants and a straight horizontal line should be obtained as the TOF versus concentration plot. Fig. 5 shows, that in the case of

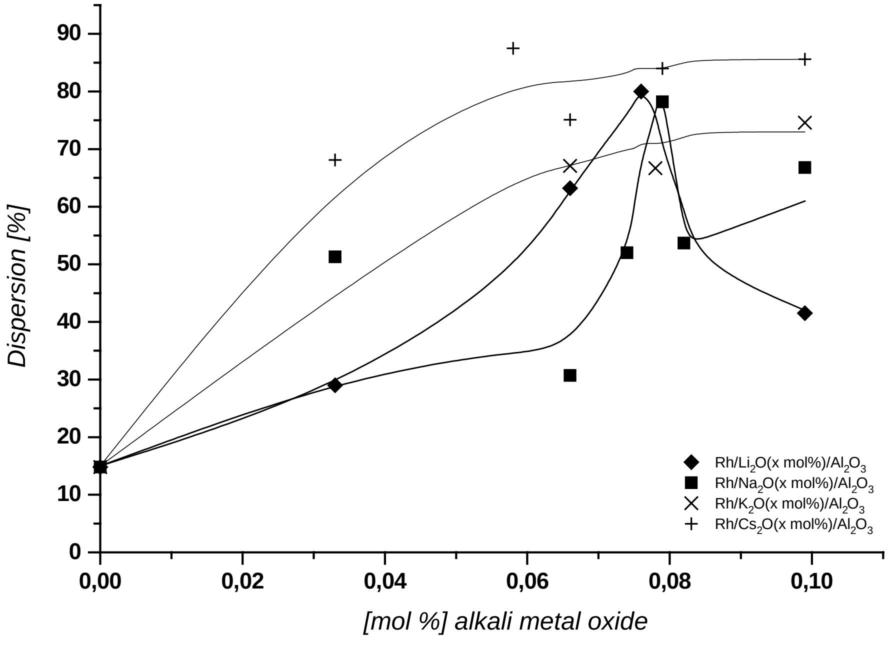

Fig. 3. Dispersion of rhodium as a function of the amount of Li, Na, K and Cs supported on γ-Al_2O_3 for Rh/alkali metal oxide/Al_2O_3 catalysts.

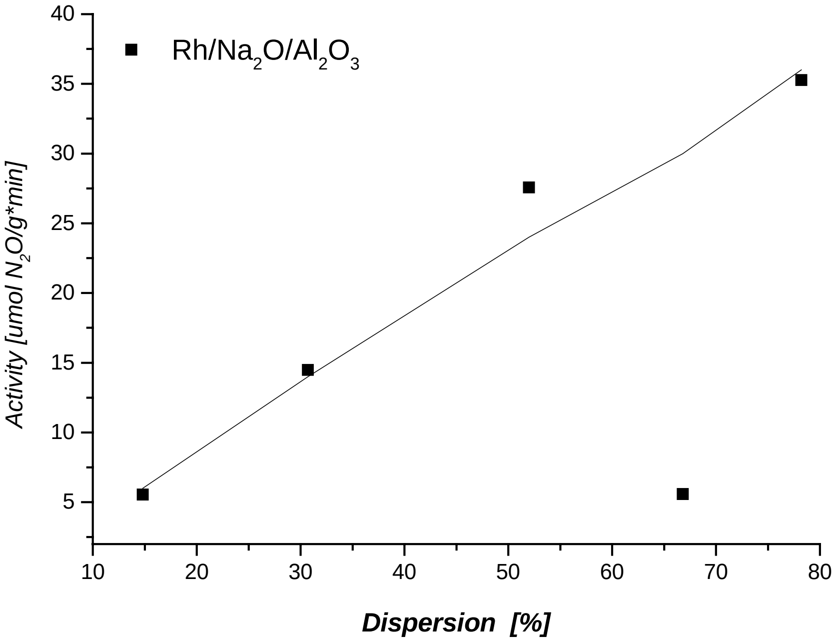

Fig. 4. Specific activity in the decomposition of N_2O as a function of the dispersion of rhodium in Rh/Na_2O/Al_2O_3 catalyst.

all samples containing less than about 0.08% of the dopant TOF is almost independent of the dopant concentration indicating that dispersion is indeed the main factor influencing the changes of catalytic activity. However, in the case of samples doped with lithium and sodium a dramatic drop of TOF takes place when the concentration of dopants becomes greater than about 0.08 mol%. A conclusion may be thus formulated that in the case of samples containing larger amounts of lithium and sodium, the latter influence the behaviour of active sites present at the surface of rhodium and decrease their specific activity or reduce their number.

A question could be raised whether the detrimental action of sodium at its higher concentration could be eliminated. This may be of great practical importance because the commercial alumina contains often the amounts of sodium corresponding to the range in which a decrease of catalytic activity is observed. Taking into account the observation that addition of potassium or cesium strongly enhance the catalytic activity in the whole range of their concentrations, an

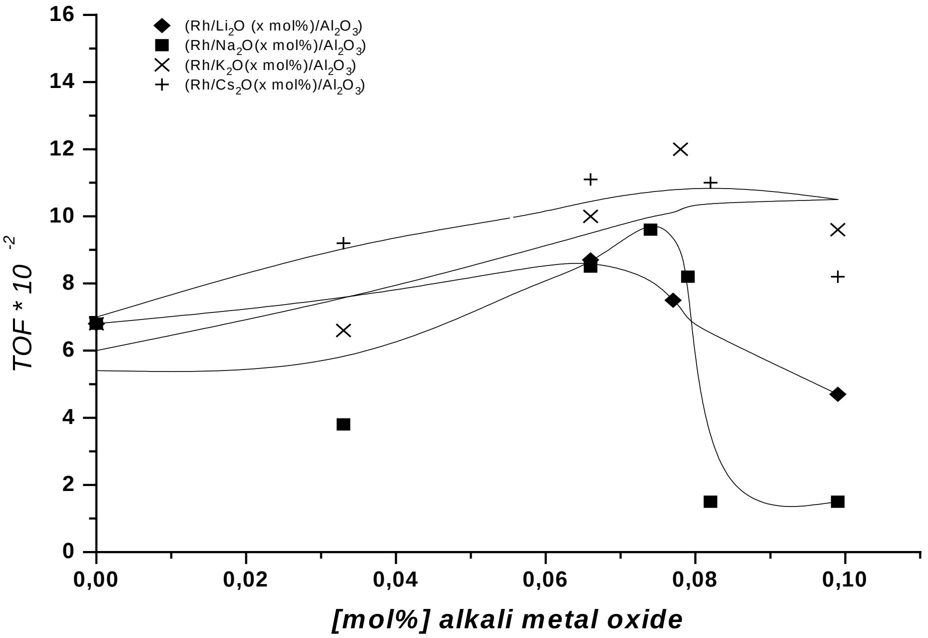

Fig. 5. TOF of N_2O decomposition as a function of the alkali metal content in the catalyst samples. Reaction temperature: 325 °C.

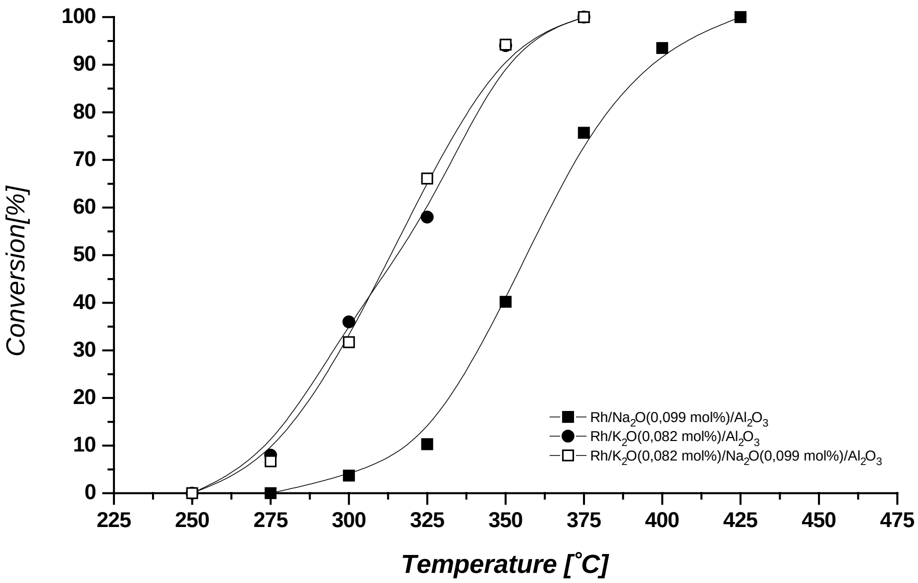

Fig. 6. N_2O conversion as a function of temperature for Na, K and K/Na containing catalysts.

experiment was carried out in which the sample containing 0.099 mol% Na_2O was doped with 0.082 mol% K_2O. Results presented in Fig. 6 clearly indicate that addition of potassium improves the catalytic activity to the same extent independently of whether it is deposited on pure alumina or alumina containing high amount of sodium. The negative influence of sodium on catalytic activity is thus compensated by the positive effect of the deposition of potassium.

Two questions arise from the experiments described in this paper. The first relates to the mechanism of the influence of deposition of alkali metals at the surface of alumina support on the dispersion of rhodium. An explanation may be considered basing on the observation that deposition of alkali metals changes a point of zero charge of the alumina support and hence modifies the process of deposition of rhodium salts in the course of the preparation of the catalysts. The second question concerns the influence of the larger amounts of lithium and sodium on the specific activity or number of active sites at the surface of rhodium particles. A marked difference between the influence of sodium and potassium is another point of general interest.

Further studies are in progress aiming at the elucidation of the above mentioned mechanisms.

4. Conclusions

- It may be concluded that two effects operate:
    - ○ influence of deposition of alkali metals on the dispersion of rhodium,
    - ○ modification of the specific activity of active sites which is reflected in the change of the TOF.
- Doping with alkali metals influences the dispersion of rhodium. In case of lithium and sodium dispersion increases and attains a maximum at surface concentration of 0.07–0.08 mol%, whereas for potassium and cesium it increases and attains the plateau at this concentration.
- The changes of dispersion are reflected in the changes of catalytic activity in the decomposition of N_2O.
- Dependence of activity on dispersion is linear for potassium and cesium, whereas in the case of sodium a dramatic decrease of activity is observed when the concentration of sodium surpasses 0.07–0.08 mol%.

References

[1] J. Pérez-Ramirez, F. Kapteijn, G. Mul, J.A. Moulijn, Appl. Catal. B 35 (2002) 227.
[2] T.W. Dann, K.H. Schulz, M. Mann, M. Collings, Appl. Catal. B 6 (1995) 1.
[3] F. Kapteijn, J. Rodriguez-Mirasol, J.A. Moulijn, Appl. Catal. B 9 (1996) 25.
[4] J.N. Armor, Y. Li, Appl. Catal. B 1 (1992) L21.
[5] J.N. Armor, T.A. Braymer, T.S. Farris, C.S. Swamy, Y. Li, F.P. Petrocelli, El. Weist, S. Kannan, Appl. Catal. B 7 (1996) 397.
[6] G. Centi, A. Galli, B. Montanari, S. Perathoner, A. Vaccari, Catal. Today 35 (1997) 113.
[7] K. Rahkamaa, T. Salmi, Chem. Eng. Soc. 54 (1999) 4343.
[8] S. Srinivasan, C.R. Narayanan, A. Biaglow, R. Gorte, A.K. Datye, Appl. Catal. A 132 (1995) 271.
[9] N. Macleod, J. Isaac, R.M. Lambert, Appl. Catal. B 33 (2001) 335.