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The catalytic activity of alumina supported Ru nanoparticles for NO/CH_4 reaction

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Alumina supported colloidal Ru nanoparticles, with an initial average size of 4.8 nm, show high activity for NO conversion for $T \geqslant 450$ °C and remarkably high selectivity ($\approx 80\%$) to syngas at 600 °C.

The reaction between NO and CH_4 is particularly interesting and worth investigation from environmental and partial oxidation of methane (POM) points of view. From an environmental point of view the catalytic reduction of NO is an important research topic. The NO/CH_4 reaction can also be of great practical interest if methane could be selectively oxidized to syngas (CO and H_2). To this point, to our knowledge, there are no published reports concerning the POM reaction using NO as an oxidant.

Ru/Al_2O_3 was selected as the catalytic system because Ru-based catalysts have proved to have good activity and selectivity for the POM reaction.[1]

The NO/CH_4 reaction is a structure sensitive reaction.[2] Therefore, the catalytic activity and selectivity are strongly related to the morphology of the supported metal particles.[3] We have recently reported that, well-structured Ru nanoparticles can be obtained by the colloid method and then supported on alumina.[4]

The aim of our investigation is to prepare a catalyst (6% Ru/Al_2O_3) by supporting uniform colloidal Ru nanoparticles on alumina and then to test the specific activity and selectivity for the NO/CH_4 reaction.

The catalyst was prepared by reduction of $RuCl_3$ with ethylene glycol in the presence of γ-alumina (Aerosil, 73 m^2 g^{-1}). The detailed preparation method for the Ru/Al_2O_3 catalyst has been described in detail elsewhere.[4] Briefly, alumina was added under stirring to an ethylene glycol solution containing dissolved $RuCl_3 \cdot 3H_2O$ (Wako Chemicals, purity >99%) in order to form a suspension. The reduction of $RuCl_3$ on the surface of alumina was carried out at 180 °C. The resulting 6% Ru/Al_2O_3 catalyst was calcined at 500 °C in air for 8 h in order to decompose the remaining ethylene glycol.

The size distribution of the alumina supported Ru nanoparticles, statistically determined from TEM micrographs, is remarkably narrow, ranging between 3 and 6 nm.[4] Additionally, the average size of the Ru nanoparticles was measured by H_2 and CO chemisorption by assuming that each exposed Ru atom adsorbs one hydrogen atom or one CO molecule (Table 1). The TEM measurements of the catalyst cycled up and down in the NO/CH_4 reaction mixture for more than 80 h in the temperature range 400–600 °C reveal an increase in the average size of the Ru particles from 4.8 to 6.8 nm.

Table 1 Average size of Ru nanoparticles, as determined from TEM micrographs and by H_2 and CO chemisorption

	Ru particle size/nm		
Catalyst	TEM	H_2	CO
6% Ru/Al_2O_3 (fresh)[a]	4.8	4.7	5.4
6% Ru/Al_2O_3 (used)[b]	6.8	—	—

[a] Catalyst calcined in air at 500 °C for 8 h after Ru colloid deposition on alumina (prior to the TPR and catalytic runs). [b] Catalyst used for more than 80 h in NO/CH_4 reaction mixture in the temperature range 400–600 °C.

The catalytic tests were performed with 0.05 g of catalyst in the temperature range 400 to 600 °C. The space velocity of the reactant mixture (1% NO, 0.55% CH_4 and balance Ar) was 60000 h^{-1} GHSV (gas hourly space velocity). The dependence of the catalytic activity on the reaction temperature for 6% Ru/Al_2O_3 is presented in Fig. 1. The conversion of NO at 400 °C is close to zero (only traces of NO decompose, for a short time, to N_2). A temperature increase from 400 to 450 °C leads to a sudden increase in NO conversion from zero to 100%. At any of the reaction temperatures, NO is selectively converted to N_2. Methane conversion to CO_x, H_2 and H_2O has an increasing trend with increasing reaction temperature. The concentration of CO increases progressively from 0.16% at 450 °C to 0.42% at 600 °C. In contrast, the concentration of CO_2 decreases from 0.23% at 450 °C to 0.1% at 600 °C. The evolution of hydrogen closely follows that of CO (increases from $\approx 0.2\%$ at 450 °C to 0.86% at 600 °C). The highest selectivity to syngas was observed at 600 °C ($S_{CO} \approx 81\%$ and $S_{H2} \approx 82\%$). A stoichiometric mixture of NO/CH_4 (1% NO, 1% CH_4) gave at 600 °C a selectivity to CO and H_2 of 99 and 95%, respectively.

It should be noted that, in the absence of CH_4, the 6% Ru/Al_2O_3 catalyst is rapidly deactivated either by air or by NO. The oxygen-deactivated catalyst can be easily reactivated in pure methane at any of the reaction temperatures. On the other hand, the catalyst working in the reaction mixture shows stable activity over time.

The TPR (Thermal Programmed Reduction) experiments were performed in order to get information regarding the active state of the catalyst. The fresh 6% Ru/Al_2O_3 catalyst (calcined in air at 500 °C for 8 h) exhibits a large TPR peak at 326 °C and a smaller one at 182 °C (Fig. 2, trace a). The high temperature TPR peak was attributed to the reduction of the RuO_2 species

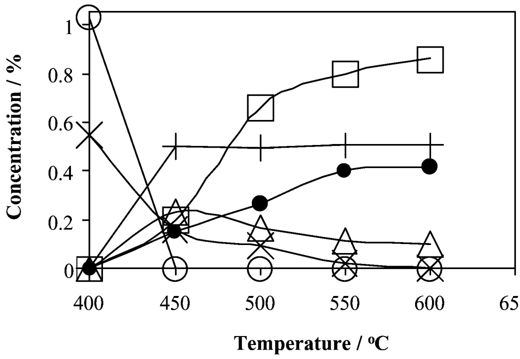

Fig. 1 The conversion of NO and CH_4 to all products as a function of temperature for 6% Ru/Al_2O_3 catalyst. (○), NO; (×), CH_4; (+), N_2; (△), CO_2; (●), CO; (□), H_2 (reaction mixture 1% NO, 0.55% CH_4 and balance Ar).

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whereas the low temperature peak was assigned to the reduction of well-dispersed RuO_x species.[5] The TPR profile of the active catalyst (Fig. 2, trace b) shows clearly that the amount of RuO_2 decreases in the reaction conditions. The high temperature TPR peak of the active catalyst at 254 °C (trace b) is smaller as compared with the peak at 326 °C of the calcined catalyst (trace a).

The XRD patterns of the oxygen-deactivated (spectrum a) and of the active (spectrum b) 6% Ru/Al_2O_3 catalyst are comparatively presented in Fig. 3. A slight increase in the intensity of the XRD peak characteristic for RuO_2 at $2\theta \approx 28°$ can be observed for the deactivated catalyst (Fig. 3, spectrum a).

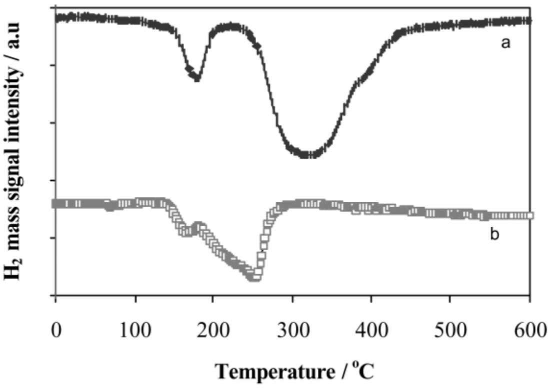

Fig. 2 TPR profiles for the 6% Ru/Al_2O_3 catalyst: (a) catalyst prepared by Ru colloid deposition on alumina, calcined at 500 °C in air for 8 h (fresh catalyst) (b) catalyst working in the reaction mixture (active catalyst).

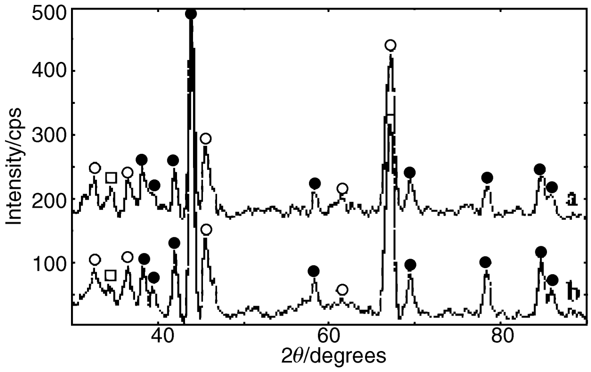

Fig. 3 The XRD patterns of the 6% Ru/Al_2O_3 catalyst: (a) catalyst deactivated by NO at 500 °C (b) active catalyst (working in the reaction mixture). (●), Ru; (□), RuO_2; (○), Al_2O_3.

Some sintering of the supported Ru particles at the elevated reaction temperature may also contribute to the differences (XRD reflections of the metallic Ru) observed between the two XRD profiles.

From the TPR and XRD measurements it can be concluded that (I) the catalytically active phase is metallic Ru and (II) the reason for the catalyst deactivation in oxidizing atmosphere is the formation of RuO_x species (mainly RuO_2) which are inactive for the NO/CH_4 reaction. However, it is clear that the active 6% Ru/Al_2O_3 contains, beside metallic Ru (main phase), small amounts of RuO_2.

There is a debate concerning the formation mechanism of CO and H_2 in the POM reaction. Some studies are supporting the idea that CO_2 and H_2O are the primary reaction products of the POM.[6] On the other hand, Hickman *et al.*[7] observed that for a short contact time (0.01 s), the primary reaction products are H_2 and CO because the secondary reactions, such as methane steam reforming or water–gas shift reactions, are slow processes. Thermodynamic calculations for the partial oxidation of methane with oxygen differ significantly from our experimental data.[8] For example at 600 °C the theoretically predicted data for the H_2/CO, CO_2/CO and CH_4/CO ratios are 2.5, 1 and 0.25, respectively whereas our experimental values for the same ratios are 1.7, 0.2 and 0 (see Fig. 1). The significant deviation of our data from the thermodynamic equilibrium values suggests that, in our experimental conditions (short contact time, 0.06 s), the distribution of the reaction products is insignificantly affected by secondary equilibrium reactions (*i.e.* methane steam and carbon dioxide reforming, water–gas shift reaction) and therefore it is likely that both CO and H_2 are the primary reaction products. It is clear that the high selectivity to CO and H_2 at low temperatures indicates that the NO/CH_4 reaction over the Ru/Al_2O_3 catalyst is occurring under non-equilibrium conditions.

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