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Formation of the rhodium oxides Rh_2O_3 and RhO_2 in Rh/NaY

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The oxidation states of Rh in NaY supported catalysts have been studied by temperature programmed reduction (TPR). After calcination of the exchanged catalyst to 380°C, both RhO_2 and Rh_2O_3 are identified, besides small amounts of RhO^+ and Rh^{3+}. Quantitative reduction is possible for samples calcined at temperatures not exceeding 500°C. Re-oxidation of the reduced samples leads to formation of RhO_2 and Rh_2O_3, with negligible protonolysis to Rh^{3+}. The dioxide prevails after re-oxidation at 320°C, but the sesquioxide after oxidation at 500°C. In the temperature regime where both oxides coexist the reduction of NO with propane is catalyzed even at an O_2/C_3H_8 ratio of 10. Total oxidation of propane reaches 80% at 350°C.

Keywords: rhodium oxides in NaY; temperature programmed reduction; NO_x reduction

1. Introduction

The propensity of rhodium to catalyze numerous important reactions, including hydrogenation and hydroformylation of olefins [1,2], conversion of synthesis gas to hydrocarbons and oxygenates [3], and reduction of nitric oxide with carbon monoxide [4], has motivated much research of Rh on a variety of supports. The majority of that work identified dispersion and structure of Rh under reducing conditions, while the oxidation of Rh^0 to Rh^+ by protons, in particular in the presence of CO, also received considerable attention [5]. Under oxidizing conditions the formation of Rh^{n+} and $[RhO]^+$ ions [6] and of the sesquioxide Rh_2O_3 [7–9] has been reported; also RhO has been identified [10]. It is surprising, however, that little mention is made in the catalytic literature of supported rhodium dioxide, RhO_2 [7], although the phase diagram of Rh–O_2 shows that in macroscopic systems this is the most stable compound over a wide range of O_2 pressures and temperatures [11].

In this paper we report on observations of both oxides, Rh_2O_3 and RhO_2, on a zeolite support. These samples were tested as catalysts using the reduction of nitric oxide with propane as the catalytic probe [12,13].

2. Experimental

2.1. CATALYST PREPARATION

Ion exchange was performed by dropwise addition of a solution of 0.86 g $[Rh(NH_3)_5Cl]Cl_2$ in doubly deionized water to a slurry of 10 g NaY from Linde in 2000 ml H_2O at 80°C under air over a period of 4 days. This was followed by washing with water until the obtained solution was chlorine-free. Under these conditions ligand exchange transforms $[Rh(NH_3)_5Cl]^{2+}$ ions to $[Rh(NH_3)_5(H_2O)]^{3+}$ ions [5]. The ion exchanged sample was dried at 120°C in air and calcined in an oxygen flow (2000 ml/g min) up to 380°C with a ramp of 0.5°C/min, followed by calcination at this temperature for 6 h. The flow was switched to Ar for 20 min and the catalyst was cooled while in the Ar flow. ICP elemental analysis showed a metal load of 3.1 wt% Rh.

2.2. TEMPERATURE PROGRAMMED REDUCTION AND OXIDATION CYCLES

After ion exchange and calcination the samples were reduced in H_2 by temperature programmed reduction (TPR) as described previously [14]. The temperature program was stopped when 500°C was reached. Following a TPR run, the sample was cooled in H_2/Ar and the flow was switched to Ar (30 ml/min) at room temperature. The hydrogen consumption was obtained by integrating the TPR profiles versus time, to achieve optimum base line corrections. These curves are reproducible within 5%; they are not shown here. The experimental error in the hydrogen consumption is ±5%. Subsequent re-oxidation was always preceded by cooling to −80°C, in order to prevent particle agglomeration upon first exposure to oxygen. After switching the gas flow to pure O_2 at 1 bar and a flow rate of 2000 ml/g min, the following reoxidation–reduction cycles were carried out:

(1) Re-oxidation up to 380°C, hold for 6 h, switch to Ar at 380°C for 20 min, 2nd TPR.

(2) Re-oxidation up to 500°C, hold for 2 h, switch to Ar at 500°C for 20 min, 3rd TPR.

(3) Re-oxidation up to 320°C, hold for 1 h, cool in O_2 flow, switch to Ar at 20°C for 1 h, 4th TPR.

2.3. REDUCTION OF NO WITH PROPANE

In the steady state plug flow mode, catalytic measurements were made using a pyrex reactor charged with 200 mg Rh/NaY zeolite on a porous frit. After ion exchange, calcination up to 380°C and reduction to 500°C, the catalyst was reoxidized up to 320°C. After pretreatment, the catalyst was heated from 20 to 300°C at 3°C/min in 30 ml/min He. Reaction studies were conducted with the inlet concentrations of 1000 ppm NO, 1000 ppm C_3H_8, 10000 ppm O_2, and He balance with a total flow of 200 ml/min. Reaction products were monitored by gas chromatography with molecular sieve 13X and Porapak Q columns (Alltech). Reaction temperature was held for 60 min then raised in 25°C intervals until 425°C. N_2 formation was used to calculate NO_x conversion. As CO formation was negligible, the evolution of CO_2 was used to calculate C_3H_8 conversion.

3. Results and discussion

The TPR profile of the sample after calcination to 380°C is shown in fig. 1a. The spectrum exhibits three hydrogen consumption peaks. Beside the most prominent peak centered at 40°C a shoulder at 150°C and a broad peak around 350°C are present.

On the basis of the reoxidation experiments we assign the dominant peak around 40°C to the reduction of rhodium oxide particles; the state of these will be discussed below. Reduction temperatures around 50°C for highly dispersed rhodium on Al_2O_3 have been observed [15]. Even reduction at room temperature for graphite-supported FeRh catalysts has been reported [16]. It was shown that such particles are formed in Rh/NaY during calcination by the sequence of autoreduction to Rh^0 followed by oxidation of Rh^0 to Rh oxide [6]. The ammine ligands of the $[Rh(NH_3)_5H_2O]^{3+}$ ions or their decomposition products are responsible for the autoreduction. At a calcination temperature of 500°C rhodium oxide particles interact with protons to form Rh^{3+} ions, which exhibit a TPR peak at 175–200°C [6]. From the dominance of the TPR peak caused by reduction of oxides it follows, that this protonolysis is small at a calcination temperature of 380°C. The assignment of the shoulder at 150°C is not entirely clear. We tentatively assign it to Rh^{3+}. The shift to a lower reduction temperature is most likely the result of Rh^{3+} remaining in the supercages after calcination. In the case of Pd/NaY it was shown that ions that remain in the supercage are reduced at a lower temperature than those which have migrated into the small cages during high temperature calcination [17]. The presence of rhodyl ions, $(RhO)^+$, which were previously identified by reduction with CO, cannot be excluded. Their reduction to Rh^+ has been found to lead to a TPR peak in the region of 70–90°C [6].

We tentatively attribute the small peak around 350°C to the reduction of the Rh^+ to Rh^0. This chemistry is under investigation in our laboratory and will not be further discussed here. After completing the TPR run up to 500°C, rhodium is completely reduced to Rh^0, as follows from the amount of hydrogen consumed given in table 1. The ratio of $H/Rh = 3.50$ indicates that besides Rh^{3+} also Rh^{4+} is present, i.e. that not only Rh_2O_3 but also RhO_2 has been formed after calcination.

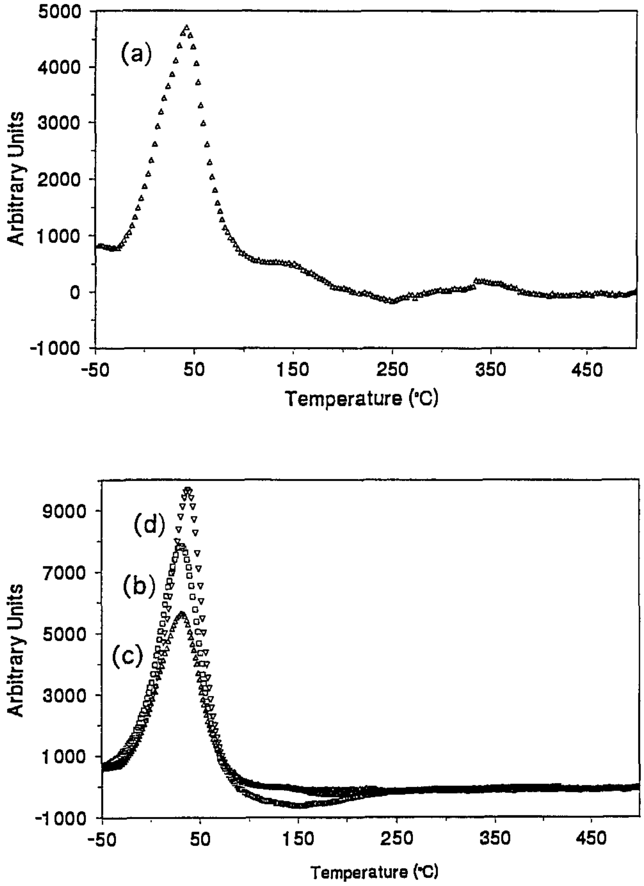

Fig. 1. (a) 1st TPR of a RhNaY sample after ion exchange and calcination up to 380°C. (b) 2nd TPR of RhNaY following the 1st TPR (a) and reoxidation up to 380°C. (c) 3rd TPR of RhNaY following the 2nd TPR (b) and reoxidation up to 500°C. (d) 4th TPR of RhNaY following the 3rd TPR (c) and reoxidation up to 320°C.

This is confirmed by subsequent oxidation of the reduced catalyst up to 380°C, followed by a second TPR run, shown in fig. 1b. Only one peak around 40°C is observed. The absence of TPR-peaks in the ionic region and the occurrence of a hydrogen desorption peak (visible as a dip in the TPR around 150°C) indicate reduction of the rhodium to metallic particles. The H/Rh ratio of 3.24 (table 1) suggests that, again, a mixture of RhO_2 and Rh_2O_3 is formed during oxidation of the sample after the first reduction. If RhO_2 or Rh_2O_3 are indeed coexisting, it follows from the phase diagram and general thermodynamic principles, that RhO_2 should prevail at lower temperature and higher oxygen pressures. We therefore varied the reoxidation temperature of reduced samples and determined the H/Rh ratio by TPR.

First, the reduced sample was re-oxidized up to 500°C. As shown in fig. 1c, the

Table 1
H-consumption per Rh-atom obtained from the integration of the TPR profiles presented in figs. 1a–1d

	1st TPR ($T_C = 380°C$)	2nd TPR ($T_{ox} = 380°C$)	3rd TPR ($T_{ox} = 500°C$)	4th TPR ($T_{ox} = 320°C$)
H/Rh	3.50	3.24	3.15	4.10

intensity of the TPR peak around 40°C is much lower than in the sample oxidized up to 380°C. Again, the rhodium is reduced to the metallic state after the TPR. The ratio of H/Rh = 3.15 in table 1 indicates that after calcination up to 500°C the dominant oxide is Rh_2O_3.

Subsequently, the sample was re-oxidized (the fourth such treatment of this sample) up to 320°C. The result, shown in fig. 1d, is a much higher TPR peak at 40°C. No ionic species reducible above 100°C are detected. In the view of the experimental error of ±5% the ratio of H/Rh = 4.1 (table 1) indicates that oxidation at 320°C produces mainly the dioxide RhO_2.

Samples after calcination to 380°C and reduction to 500°C were inspected by TEM; no particles larger than the supercages were observed. The present TPR results indicate that for such particles the dioxide, RhO_2, is stable at 320°C, but the sesquioxide, Rh_2O_3, is more stable at 500°C. While this is similar to the stability sequence indicated by the phase diagram for macroscopic samples [11], it appears that the transition between the oxides is shifted to lower temperature, from 700 to 500°C, for the small particles in the present samples. The apparent co-existence of both oxides after oxidation up to 380°C in NaY supported Rh can be explained by assuming that there is a particle size distribution; it thus appears possible that with increasing temperature the conversion of RhO_2 to Rh_2O_3 starts with the smallest particles.

Nitric oxide reduction to N_2 and propane conversion to CO_2 versus temperature are shown in fig. 2. Nitric oxide conversion reaches a maximum at ca. 335°C, when 29% of NO_x is converted to N_2. The selectivity (NO_x converted/C_3H_8 converted) decreases with temperature; it is 0.56 at 325°C, when 28% NO_x is converted to N_2 while less than 50% of propane is oxidized, whereas at 335°C the selectivity is 0.36. These results suggest that the valence change between Rh^{4+} and Rh^{3+} is fast enough to catalyze a redox process such as the oxidation of propane by both O_2 and NO. However, TPR data of the used catalyst suggest that after reduction times of 4–5 h rhodium oxide particles have disintegrated to RhO^+, which also might be able to undergo valence changes other than those between Rh^{3+} and Rh^{4+}. In any case, zeolite supported Rh can thus be added to the list of catalysts for NO reduction.

At a given temperature the activity decreases with time on stream at about 10%/h. Formation of coke, also indicated by postreaction-TPR, may be a contributing factor in this deactivation; whether the formation of RhO^+ ions can also

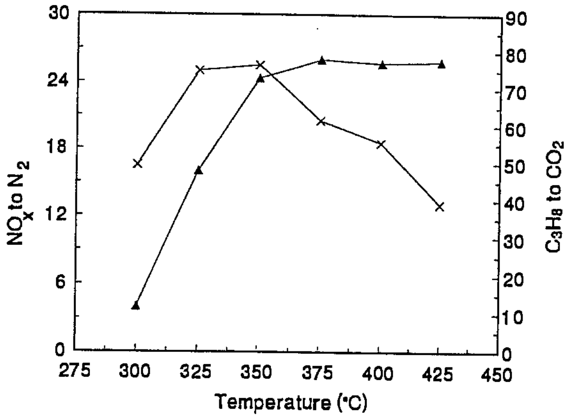

Fig. 2. Reduction of NO_x with propane as a function of temperature. Initial conversion of NO_x : (×). Initial conversion of propane: (▲).

rationalize deactivation has not been clarified yet and is under investigation in our laboratory.

4. Conclusions

Rhodium in NaY is quantitatively reduced with H_2 to Rh^0, if the previous calcination temperature does not exceed 500°C. Oxidation of the reduced Rh in O_2 at 1 bar results in formation of two oxides; at a temperature near 320°C the dioxide RhO_2 prevails; at higher temperature increasing amounts of the sesquioxide Rh_2O_3 are formed, it prevails after oxidation at 500°C. The oxidized catalyst is able to catalyze NO reduction with propane above 300°C. The selectivity for propane to react with NO rather than with O_2 is lower than for Cu/ZSM5 [18]. The selectivity decreases upon coke formation and (or) when Rh oxide particles are slowly converted to Rh ions.

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