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Carbon-Based Ruthenium Catalyst for Ammonia Synthesis Doped with Caesium Nitrate. Studies of the Catalyst Activation

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Ruthenium catalysts supported on carbon and promoted with caesium are known to be extremely active in NH_3 synthesis [1–7]. Typically, caesium nitrate is used as the Cs precursor for the catalyst preparation [3–5]. Prior to the NH_3 synthesis, the $CsNO_3$-Ru/C system is activated (reduced) in a hydrogen containing stream. This leads both to the reduction of the Ru surface and to the caesium salt decomposition. The activation process has been poorly understood so far. Consequently, the form (forms) of the caesium promoter in the catalyst operating under ammonia synthesis conditions as well as the promoting mechanism of caesium still remain unclear.

This communication is concerned with the activation (reduction) studies of the $CsNO_3$-Ru/carbon catalyst precursor by the temperature-programmed technique (TPR-MS), the measurements being supplemented by the oxygen chemisorption experiments. The TPR-MS studies have shown that ruthenium facilitates the caesium nitrate decomposition, *i.e.* the $CsNO_3$ decomposition starts at about 100°C for $CsNO_3$-Ru/C, while for the ruthenium-free $CsNO_3$/C reference sample it starts at about 400°C. The chemisorption studies have shown, in turn, that the oxygen consumption for caesium promoted Ru/C specimen is by several times larger than that for the unpromoted one (Ru/C), thus, indicating that caesium exists in a highly reduced state after the catalyst activation.

The $CsNO_3$-Ru/C catalyst was prepared according to the conventional procedure [3,4]. A batch of the graphitized carbon support (extrudes of 0.8 mm in diameter, 66 m^2/g [8,9]) was impregnated with a THF solution of ruthenium carbonyl, followed by drying in air at 60°C and reduction in flowing hydrogen of high purity (99.9999%). The ruthenium loading in the unpromoted Ru/C sample was 9.1 wt. %. Subsequently, Ru/C was impregnated with an aqueous solution of caesium nitrate and dried in air at 90°C. For $CsNO_3$/C, the carbon support was impregnated with a $CsNO_3$ solution. The Cs/C weight ratios in the prepared samples were 0.22 gCs/gC and 0.19 gCs/gC for $CsNO_3$-Ru/C and $CsNO_3$/C, respectively.

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The TPR studies were performed in a tubular flow reactor using 6% H_2/Ar or 80% H_2/Ar gas mixtures (40 ml/min). The reactor outlet was connected with the heated sampling valve of a Dycor Ametek MA200 quadrupole mass spectrometer that allowed 12 mass signals to be recorded simultaneously. The temperature of the reactor was increased up to 430°C (at a 10°C/min ramp), whereupon the reduction of the sample at 430°C was continued for further 18 h. Hence, the temperature programme of the activation corresponded to that applied in the NH_3 synthesis tests performed previously in our laboratory [3,4] with the caesium promoted catalysts. In order to determine the changes in relative amounts of various released gaseous species and to separate such contributions, the obtained mass spectra were elaborated in terms of standard mass spectra of respective compounds.

To determine the oxygen chemisorption, the reduced sample was first cooled to 400°C in a hydrogen–argon mixture and then flushed with helium for 30 min to remove hydrogen, followed by cooling in helium to 0°C. The oxygen consumption was measured at 0°C by the pulse method, introducing small O_2 portions (2 μmol) into the helium stream until saturation was reached.

The most relevant results of the TPR-MS studies are presented in Figs 1 and 2: the changes in concentrations of the abundant compounds (arbitrary units) are plotted *vs.* the activation time. Fig. 1 corresponds to the $CsNO_3$-Ru/C catalyst and Fig. 2 is referred to the $CsNO_3$/C sample, both experiments being performed with the 6% H_2/Ar mixture.

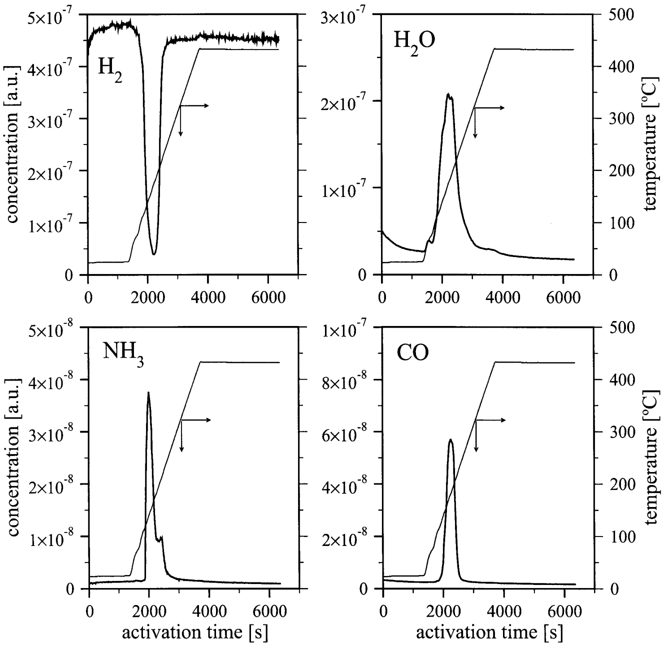

Figure 1. TPR-MS studies of the $CsNO_3$-Ru/C catalyst: concentrations of the main components in the outlet gas stream (6% H_2/Ar, 40 ml/min) *vs.* time of the experiment; the starting catalyst (0.2585 g) contained 0.1822 g C, 0.0182 g Ru and 0.0581 g $CsNO_3$.

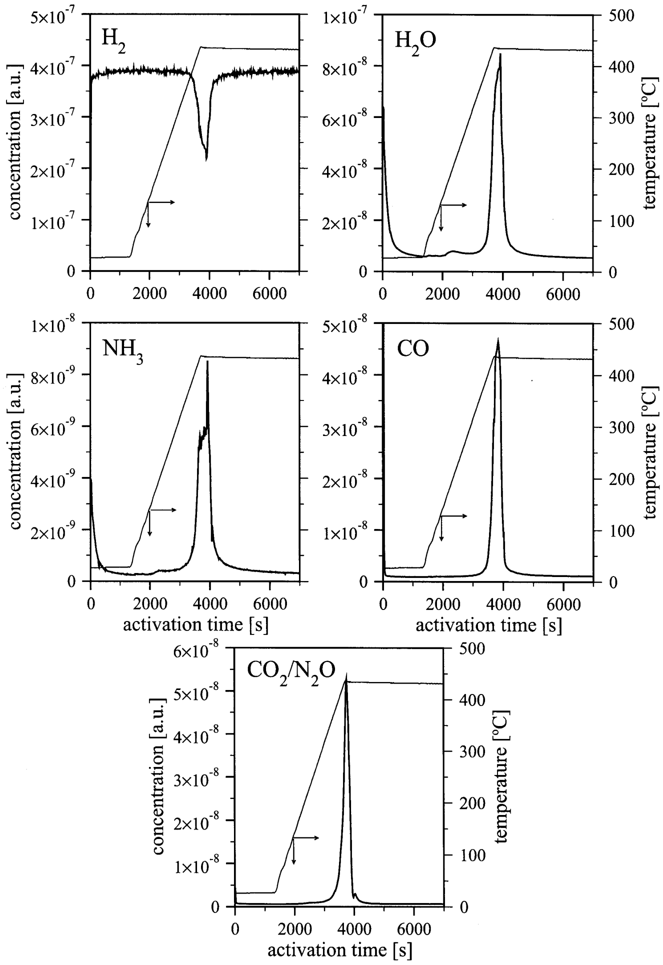

Figure 2. TPR-MS studies of the $CsNO_3$/C sample: concentration of the main components in the outlet gas stream (6% H_2/Ar, 40 ml/min) *vs*. time of the experiment; the starting sample (0.2332 g) contained 0.01822 g C and 0.0510 g $CsNO_3$.

As seen in Fig. 1, the interaction of hydrogen with the $CsNO_3$-Ru/C catalyst begins at about 100°C (a H_2 consumption peak) and is accompanied by the evolution of water vapour, ammonia and carbon monoxide as the main reaction products. Small amounts of nitrogen, carbon dioxide and methane have also been detected in the effluent gas (not presented in Fig. 1). Analogous trends in evolution of MS signals were found, when the reactor was supplied with a 80% H_2/Ar mixture. However, in that case, the changes in the H_2 and NH_3 concentrations were limited to a narrower temperature range.

The above-mentioned results demonstrate that nitrate anions in $CsNO_3$ are reduced with hydrogen to ammonia mainly (the N_2 signal is considerably smaller than that of NH_3). This is in accord with the literature data obtained for $CsNO_3$-Ru/MgO and several model systems [10,11]. A pronounced peak of the CO evolution (see Fig. 1) indicates that the oxygen-containing complexes are formed on the carbon surface, most likely as a result of the carbon surface oxidation by the caesium nitrate decomposition products.

In contrast to $CsNO_3$-Ru/C, the $CsNO_3$/C material is stable in a 6% H_2/Ar stream up to about 400°C (see Fig. 2). Furthermore, the NH_3 evolution and H_2 consumption peak areas are much lower than those for $CsNO_3$-Ru/C although the $CsNO_3$ contents in both starting materials were close to each other. This means that the $CsNO_3$ decomposition in the $CsNO_3$/C sample has not been completed. Finally, large amounts of CO_2 or N_2O or both (CO_2 and N_2O are hardly distinguishable by MS) appear in the effluent gas during $CsNO_3$/C activation.

The data presented in Figs 1 and 2 show clearly that ruthenium promotes the $CsNO_3$ decomposition in hydrogen, most likely *via* the atomic hydrogen formation [12]: the hydrogen atoms adsorbed on the Ru surface spill over the carbon support and, due to high reactivity, they interact with the $CsNO_3$ phase even at a temperature as low as 100°C. The question arises, however, as to the chemical form of the caesium promoter in the reduced Cs-Ru/C catalyst. Table 1 gives the results of oxygen consumption measurements for the unpromoted (Ru/C) and Cs promoted (Cs-Ru/C) samples after their prolonged activation in the 6% H_2/Ar and 80% H_2/Ar streams, respectively.

Table 1. Oxygen consumption for the Ru/C and Cs-Ru/C catalysts.

catalyst	6% H_2/Ar activation		80% H_2/Ar activation	
	O_2 uptake [μmol/g_{Ru}]	FE_{Ru}* [%]	O_2 uptake [μmol/g_{Ru}]	FE_{Ru}* [%]
Ru/C	930	17	880	16
Cs-Ru/C	2800	–	4230	–

* Fraction exposed: number of surface Ru atoms referred to the total number of Ru atoms.

As one may notice, the O_2 "uptakes" for the caesium containing system are by several times larger than those for Ru/C, thus indicating the Cs species to react with molecular oxygen. Since CsOH is inert to O_2, the catalyst surface is probably covered partly with atomic caesium, as suggested previously [4], or, with the Cs_xO_y groups that are able to bind oxygen. Unfortunately, it is impossible to distinguish at present between Cs° and Cs_xO_y. The studies of interaction between the reduced Cs-Ru/C catalyst and water vapour (in progress) should give a more decisive answer as to the Cs state when operating.

Acknowledgments

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