Catalysis by a Ruthenium Complex Heterogenized in Faujasite-type Zeolites: the Water Gas-shift Reaction

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Summary The $Ru(NH_3)_6{}^{3+}$ complex, exchanged as such in faujasite-type zeolites, can be converted into another kind of complex of the form $[Ru(NH_3)_x(OH)_y(CO)_z]^{n+}$ with $n < 3$; this complex has no homogeneous equivalent, it is stable up to 280 °C, is a very active catalyst for the water gas-shift reaction, and it exceeds the activity of a commercial copper based low-temperature shift catalyst.

The water gas-shift reaction (1) is of considerable industrial

$$H_2O - CO \rightleftharpoons CO_2 + H_2 \qquad (1)$$

importance for the production of hydrogen and synthesis gas of any composition. Its equilibrium constant increases with decreasing temperature.[1] High conversions per pass are only possible at low temperatures and very active catalysts are therefore needed. Commercially available low temperature water gas-shift catalysts are copper based. They show appreciable activity in the 175—350 °C temperature range.[2] Recently attempts have been made to use homogeneous catalysts such as rhodium carbonyl iodide[3] $[Rh(CO)_2I_2]^-$ and ruthenium carbonyl $[Ru_3(CO)_{12}]$ in alkaline solution.[4] The number of hydrogen molecules produced per hour and per metal atom on the Ru catalyst was reported to be 0·259 at 120 °C. For the Rh catalyst it was calculated to be 0·363 at 90 °C. The disadvantage of these catalysts is that they are only stable in a very restricted temperature range. It is therefore impossible to use them in a continuous operation at high throughputs and high conversions, which require relatively high temperatures.

We report here on a ruthenium complex heterogenized in zeolites X or Y. Using this catalyst, the number of molecules of hydrogen produced per hour and per Ru atom is 0·765 at 120 °C. This catalyst is superior to the conventional copper based catalyst and remains stable in the temperature range 100—280 °C.

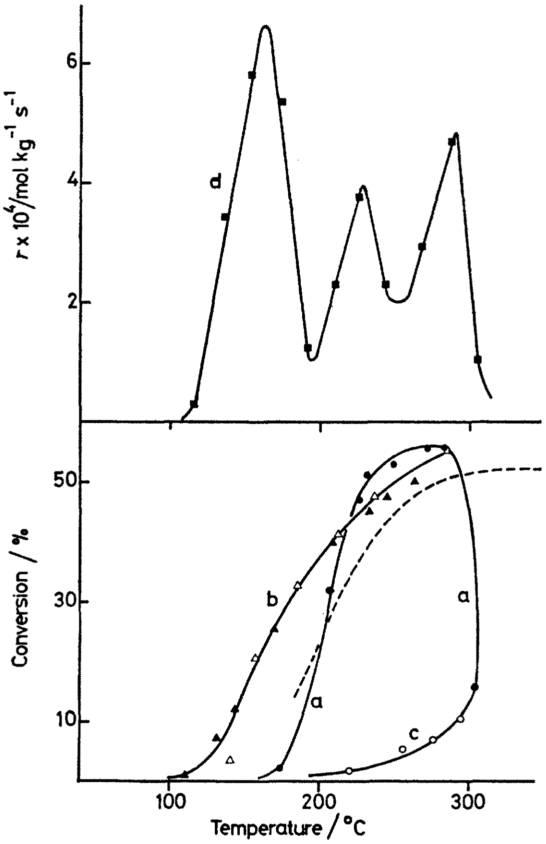

FIGURE. Catalytic activity for the water gas-shift reaction of Ru-X with respect to the oxidation state of Ru. (a), Conversion upon activation of the reactants. (b) Conversion after activation at 280 °C at increasing (△) and decreasing (▲) reaction temperatures. (c) Conversion after activation at 300 °C. (d), Rate of hydrogen uptake (r) during a temperature programmed reduction experiment.

NaX and NaY zeolites were ion-exchanged with $Ru(NH_3)_6Cl_3$ solutions giving materials with the following anhydrous unit cell compositions: RuY, $Na_{34·6}Ru_{7·1}(AlO_2)_{56}(SiO_2)_{136}$; RuX, $Na_{46·3}Ru_{13·2}(AlO_2)_{86}(SiO_2)_{106}$. The experiments were carried out in a continuous flow reactor operating at atmospheric pressure and using stoicheiometric amounts of the reactants, diluted with helium. The gaseous hourly space velocity for CO was 235 h^{-1}. The freshly exchanged zeolite was activated by heating it while the reactants were passed over it.

During thermal activation of the catalyst, an activity, pattern, shown in curve a, is found (Figure). At the same time the colour changes from white over purple to yellow at the activity maximum. Once the activity has declined again, the colour of the sample changes to dark brown. At this stage of thermal treatment, the water gas-shift activity is lost irreversibly (curve c). After suitable activation of the Ru zeolite (240—280 °C), a stable activity is reached; curve b is followed by either decreasing or increasing the catalyst temperature. The catalyst is more active than a commercial copper based, low-temperature shift catalyst (Figure, ---).

A temperature programmed hydrogen reduction of the freshly prepared Ru zeolites reveals the existence of three maxima in the rate of hydrogen uptake (r) (Figure d). The average valency of Ru after each maximum is shown in reaction (2) which suggests that the active intermediate is a

$$Ru^{III} \xrightarrow{150\,°C} Ru^{II} \xrightarrow{220\,°C} Ru^{I} \xrightarrow{290\,°C} Ru^{0} \qquad (2)$$

complex derived from $Ru(NH_3)_6{}^{3+}$, in the oxidation state either Ru^I or Ru^{II}, or a mixture of both.

Quantitative i.r. spectroscopy has shown that the catalyst undergoes the following modifications during activation: (i) The reaction shown in equation (3) occurs at

$$[Ru(NH_3)_6{}^{3+} + H_2O \longrightarrow [Ru(NH_3)_5(OH)]^{2+} + NH_4{}^+ \qquad (3)$$

75 °C at an appreciable rate and has been proposed earlier by other authors for similar zeolites.[5,6]

(ii) NH_3 is still present in the co-ordination sphere [$\delta_{sym}(NH_3)$, 1330 cm^{-1}].

(iii) Ammonia is partially replaced by CO, giving species of the types $Ru^{II}(CO)_2$ (ν_{CO} 2050 and 1960 cm^{-1}) and $Ru^{I}(CO)_2$ (ν_{CO} 2085 and 2020 cm^{-1}).

All these observations tend to indicate the existence of a complex of the type $[Ru(NH_3)_x(OH)_y(CO)_z]^{n+}$ with $n > 3$. This complex is stabilized in the zeolite supercages and has no homogeneous equivalent. It appears that product formation occurs in several steps with the catalytically active species alternating between Ru^{II} and Ru^{I}.

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