Ruthenium supported on zeolite A: preparation and characterisation of a stable catalyst for ammonia synthesis

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Reaction of $Ru(NH_3)_6Cl_3$ with Na-A and K-A zeolites yielded oligomeric amino-oxo-complexes supported on the zeolite. Controlled thermal activation under hydrogen converted the precursor in a two-step reaction into an active catalyst with good long-term stability and resistance against small doses of oxygen poison. Several nanometers sized Ru metal particles are chemically bonded to the zeolite surface which provides in the K form an alkali promoter at the metal–zeolite interface. Extensive oxidation breaks the metal–support anchoring and re-reduction produces Ru metal particles sintering rapidly into large metal crystals with only small residual catalytic activity.

Keywords: Ammonia synthesis; supported ruthenium catalyst; dispersed ruthenium; instationary kinetics; lifetime effects; ruthenium oxidation; surface analysis; XPS

1. Introduction

Ammonia synthesis over Ru is for several reasons a desirable alternative to the conventional iron system [1] which has led to the BP/Kellog catalyst using Cs promoted Ru on special carbon supports [2]. Ru catalyses oxidation and methanation of carbon which is hence considered not to be an ideal support material. Attempts were made to replace carbon by an inorganic and structurally stable support such as a zeolitic system [3]. The first zeolite Y-Ru samples were of interesting activity but of insufficient stability due to segregation of the internal Ru onto the outer surface with subsequent sintering.

Two zeolite A samples in the Na and in the K exchanged forms were used for the present catalyst preparation. Reduction of the internal pore size below the critical radius for Ru exchange of the K form should lead to a supported system. In addition, a promoter effect of K on the ammonia synthesis performance was expected. The desired catalyst is Ru supported on a zeolite in order to study the chemical differences of Ru inside a zeolite [3] (such as Na-Y) and on the outer surface of a zeolite with a chemical environment as similar as possible. The system should further allow to investigate details of the Ru–zeolite chemical interaction as in a supported catalyst the interface is much more accessible to surface spectroscopy as in the three-dimensional intercalated case. Such a study was already performed in a detailed way on a Ru-Y sample used for CO hydrogenation [4]. In a different recent approach a catalyst with Ru on zeolite A was obtained [5] by adding a Ru compound to the synthesis mixture of the zeolite. This system proved to be useful also in CO hydrogenation, a reaction in which Ru zeolites were mostly investigated before.

2. Experimental

Catalysts were prepared in 5 g batches from commercial zeolite A (Union Carbide) and $Ru(NH_3)_6Cl_3$ in aqueous solutions. The Na form was used as delivered (after elemental analysis showed the correct content of 12.3 at%), the K form was prepared by exchange with KCl and subsequent washing until all Cl^- was removed. 89 mmol of Ru complex were used in 162 ml deionised water at 333 K. Reaction times were 18 h for the K-A sample and 96 h for the Na-A sample. Both samples were dried in oil-free vacuum at 300 K for 24 h. At this stage the materials were dark-pink in colour.

X-ray diffraction data were collected in focussing Bragg–Brentano geometry with samples in 0.3 mm Lindemann tubes using monochromated Cu radiation.

TEM morphologies were analysed in a Siemens Elmiskop 102 instrument at 100 keV. Samples were suspended from a slurry in water onto carbon-coated copper grids and pre-dried before insertion in the microscope vacuum. Small electron doses at the areas photographed were used to minimise beam damage of the zeolites. Nitrogen surface areas were calculated from full BET isotherms measured with the dynamic method (Quantasorb instrument), samples were pretreated at 510 K for 16 h in a stream of N_2/He (9 : 1). Metal areas were determined from hydrogen chemisorption at 300 K and atmospheric pressure following a sample pretreatment similar to the catalyst activation procedure (slow heating to 720 K).

Kinetic testing was done in a 6 mm stainless steel reactor with 158 mg loose catalyst samples using a stoichiometric purified feed and pressures between 1 and 20 bar. The samples responded instantaneously to parameter changes, nevertheless each data point was monitored for 24 h at steady state. Activation of the catalysts was performed in synthesis gas with the following temperature program: 2 h at 300 K, heating to 620 K with 50 K/h, holding at 620 K for 1 h, second heating to 720 K with 15 K/h, holding at 720 K for 10 h. XPS data were collected in a Leybold LHS 12 MCD system with Mg radiation (240 W). The analyser was operated at

78 eV pass energy yielding a resolution of 0.78 eV at Au 4f 7/2 (84.0 eV). Samples were deposited as thin continuous films on stainless steel holders by evaporating a slurry of the zeolites in dried pentane. Only this procedure gave reproducible spectra and intensities. Sample treatments at atmospheric pressure were conducted in the attached preparation chamber. The procedures for activation were stoichiometric N_2 to H_2 feed with a temperature ramp of 50 K/h up to 720 K and 6 h holding, for oxidation a treatment in pure oxygen at 720 K for 1 h was chosen and re-reduction was done like the activation procedure with an increased holding time of 12 h. The pressure in the analysis chamber was 1 min after sample transfer in the 10^{-10} mbar range. Charging corrections were employed using the Si 2s core level as internal standard. In independent flood gun experiments (which tend to reduce the samples and can therefore not be applied with metal-loaded materials) binding energy minima at 153.5 eV were found in good agreement with the literature [6].

3. Results and discussion

3.1. SURFACE AREA

The BET nitrogen surface area of the starting material was 651 $m^2\ g^{-1}$. After exchange with K the internal surface was blocked [7] and the external surface area of the material yielded the value of 9.8 $m^2\ g^{-1}$. Loading with Ru resulted in an elemental content (by RFA) of 1.8 at% in both samples and in surface areas of 501 $m^2\ g^{-1}$ for Na-A and 6.5 $m^2\ g^{-1}$ for K-A. Both values are indicative of a particulate morphology of the Ru blocking some channels of the internal surface in Na-A and reducing external roughness in K-A. A thin continuous film of the Ru compound would have blocked all internal surface in Na-A and left the external surface area unchanged in K-A. Powder XRD showed no diffraction of the material which is not due to the low abundance (0.5 wt% Si in the sample as internal standard were well detectable) but to the poor crystallinity and/or particle size of the Ru compound. The diffraction pattern of the starting zeolite was unchanged both in line positions and relative intensities. TEM showed no contrast of the Ru material in the as-loaded state as long as the electron dose was kept low.

The hydrogen metal area after activation under synthesis conditions gave a value of 1.3 $m^2\ g^{-1}$ well in agreement with a particulate nature of the activated Ru. Metal dispersions of 17% result from the numbers given.

These observations allow to conclude that the catalyst is a supported metal type with the internal surface of the zeolite not participating in the fixation of the Ru.

3.2. ACTIVATION

In order to develop the activation program, TPD and TPR experiments were performed in Ar or in H_2 respectively. TPD showed two emission processes arising from water and eventually ammonia terminating at 500 K and from the decomposition of ammonia ligands into nitrogen and hydrogen terminating at 620 K. Stripping off the ligands is greatly facilitated in hydrogen where a single event is observed at 390 K. At this temperature the reduction of ruthenium red, an oxygen-bridged trimer of the starting amino complex was observed in a reference experiment.

The catalyst activation program ensures complete removal of all ligands (amino and oxo) from the precursor compound. The colour of the starting zeolite and the TPR are in agreement with the assumption that the originally monomeric (yellow) Ru complex underwent oxidative oligomerisation during catalyst preparation.

3.3. CATALYTIC PERFORMANCE

The kinetic data are reported for the K-A-Ru system only, as the main features were similar for both materials. The promoter effect of the alkalis could not readily be quantified since a promoting effect of Na could not be clearly established.

Fig. 1 shows a series of conversion versus temperature experiments with the total flow rate as parameter. It can be seen that all curves consist of a kinetically controlled branch at low temperatures and a thermodynamically controlled branch at high temperatures with the transition temperature lowering for lower flow rates. When plotting the logarithm of the rate of NH_3 formation versus the logarithm of the exit partial pressure of NH_3 horizontal lines were obtained for tem-

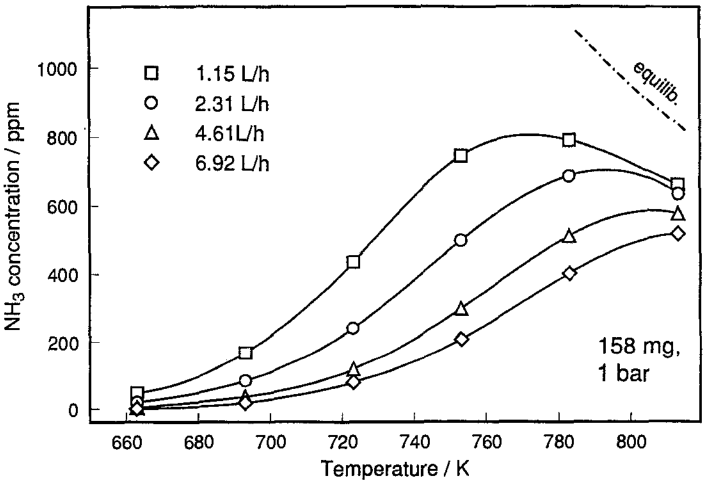

Fig. 1. Conversion versus temperature plots of the K-A-Ru sample in ammonia synthesis. Parameter is the total flow rate, 0.158 g catalyst were loaded. The equilibrium curve was calculated for 1 bar total pressure and stoichiometric feed.

peratures of 693 and 723 K corresponding to conditions far from equilibrium. Hence the reaction order is zero in ammonia in agreement with results for Cs promoted Ru on alumina [8].

Activation energies determined at 1 bar and at 20 bar pressures and at 2.31 ℓ/h were the same and with 120 kJ mol^{-1} well within the range of other K promoted Ru catalysts (Al_2O_3-K-Ru 112.9 kJ mol^{-1}) [9]. Unpromoted Ru on alumina was reported [4] to exhibit an activation energy of 71 kJ mol^{-1}. As all compared systems are supported catalysts and only present on external surfaces it may be concluded that the present catalysts are promoted by the alkali ions present in the zeolite which would require migration of some cations to the outer surface. The XRD data indicated the presence of some amorphous material after cation exchange which would allow to rationalize how excess alkali can be present on the external surface.

The long-term stability of the catalyst was tested with several reproduction batches of the K-A-Ru type. One example is given in fig. 2 which shows a conversion versus time curve after the catalyst had been on stream for 700 h and two temperature programs between 500 and 810 K had been performed. The shape of the curve illustrates the rapid response of the catalyst to parameter changes, the stability of the conversion under steady state conditions and the relative insensitive response to a feed interrupt after power failure causing uncontrolled cooling and contamination of the reactor. The high temperature at which this long-term test was performed underlines the good structural stability of the active Ru particles. The fact that after 275 h the initial activity is also retained at 695 K illustrates that the stability is not an artefact caused by the operation of the catalyst near equilibrium conversion.

Instationary conversion experiments with the conventional promoted iron cata-

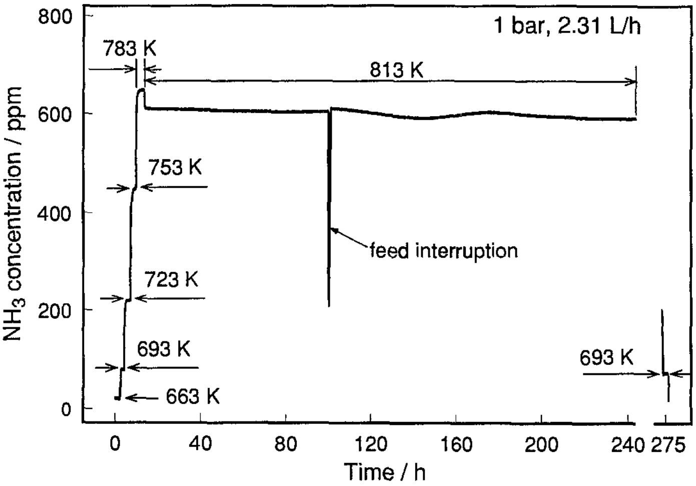

Fig. 2. Long-term stability test of K-A-Ru after 1 month on stream.

lyst [10] showed clearly that the catalyst can store nitrogen in the form of a metastable nitride but cannot store hydrogen [4]. A similar storage experiment was also performed with the present catalyst. The result is displayed in fig. 3. From the changes of feed gases it emerges that the system cannot store chemically hydrogen (eventually present molecular hydrogen or nitrogen in the pores of the zeolite excluded) but contains a large number of nitrogen atoms chemically bonded to the catalyst which can be hydrogenated. The slow changes beyond 50 min are attributed to the presence of the zeolite support which can store ammonia through its acid sites: these molecules are only slowly given off in the "inert" gas mix Ar/H_2 and the emptied sites require first re-adsorption of freshly formed ammonia after changing back to normal feed. The intensity of the ammonia pulse after feeding pure hydrogen was found to depend on the loading time with nitrogen; doubling the loading time increased the pulse from 117 to 369 ppm. Integration of the ammonia peaks allowed to conclude that the location of the nitride may be the surface of the Ru particles and does not require the existence of a metastable bulk-nitride, as the total number of ammonia molecules was always significantly less than the number of surface atoms based on the data presented in section 3.1.

Finally, the stability of the catalyst against oxygen poisoning was tested. In one experiment pulses of 1 ml oxygen were added to the feed and the response was monitored. As can be seen from the inset of fig. 4 this treatment caused a short pulse of ammonia (and probably of water which was detected due to cross-sensitivity of the NDIR detector used) with very little effect on subsequent conversion. This finding was reproduced over the whole temperature regime investigated and is in marked contrast to the iron catalyst system which is severely affected by such treatment for a prolonged time at high temperature and permanently damaged at temperatures below 660 K.

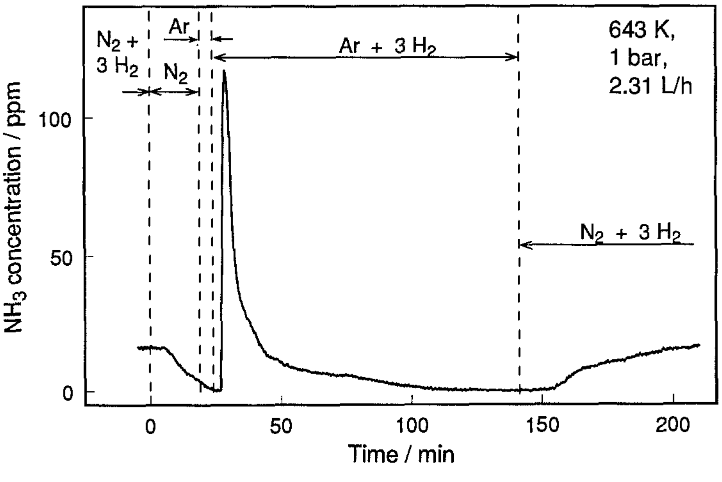

Fig. 3. Storage experiment for K-A-Ru. The changes of gas compositions are indicated.

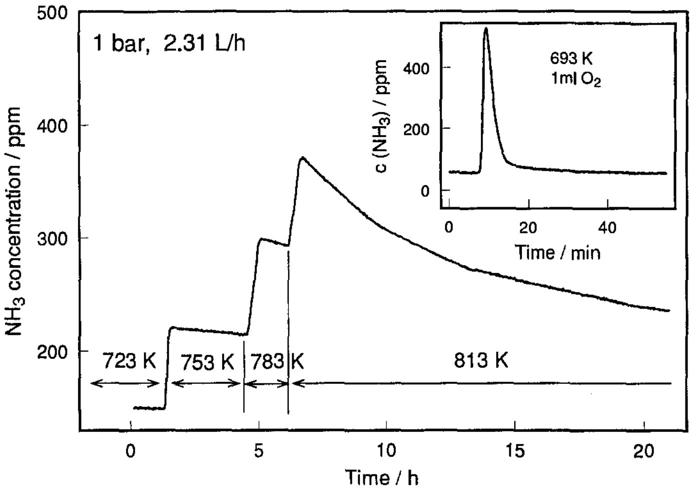

Fig. 4. Stability of K-A-Ru against oxygen poisoning. The inset shows the response to a 1 ml oxygen pulse added to the feed. The main trace indicates deactivation of a fully oxidised and re-reduced sample.

The resistance of the catalyst to short oxygen exposure is no longer existent after extensive oxidation. One catalyst batch was oxidised at atmospheric pressure for 1 h at 720 K. Afterwards a subsequent re-activation procedure (see Experimental) caused the activity to return to about 30% of the initial level. The stability of the catalyst conversion was, however, lost irreversibly as can be seen from the main curve in fig. 4. Rapid deactivation occurred at a temperature level where before the oxidation complete stability was observed (compare to fig. 3).

The deactivation behaviour is similar as found previously with a zeolite-Y-Ru ammonia catalyst [11]. In this study agglomeration of the active phase was made responsible for the effect. This would imply that moderate oxidation has little effect on the present catalyst as it does not oxidise the bulk of the metal particle. Massive oxidation leads, however, to the formation of oxides and destroys the linkages between active phase and support. This destruction is irreversible by reductive treatment which produces metallic Ru with insufficient linkages to the support.

X-ray diffraction of a re-reduced sample after the extensive oxidation treatment showed indeed clear and sharp reflections (observed were the (100), (002) and (101) reflections) of metallic Ru in addition to the unaffected zeolite pattern. The agglomeration must be extensive as the average metal particle size was found from XRD linebroadening to be 41 nm.

3.4. SURFACE ANALYSIS

XPS data were collected from the as-prepared catalysts, from samples after microreactor testing and from samples treated in the high-pressure preparation chamber of the spectrometer in order to mimic the processes in the microreactor without having to transfer the samples. In a previous paper [11] it was shown that the post mortem samples from the microreactor and the simulated samples had exactly the same XPS parameters. For this reason the analysis here focusses on the as prepared samples and on one series of in situ treatment of K-A-Ru.

Table 1 summarizes the surface compositions of the precursor samples which are both rather similar in their surface composition. The cation exchange left a measurable amount of Na on the K-A sample. The bulk elemental ratios for O : Si (4.0), Si : Al (1.0) and Ru : Si (0.2) assuming a homogeneous material, deviate significantly from the ratios detected. The character of the surface is a Ru–aquo/hydroxo complex with some amino ligands (same binding energy as ammonia adsorbed on Ru metal [12]) supported on a water film. This is not surprising as the zeolite surface binds strongly water forming a multilayer film stable enough to withstand evacuation at 300 K. The atomic ratio N : Ru is close to 1 and hence far away from the ratio of the starting compound (6) indicating extensive ligand exchange reactions taking place during preparation [13]. The XPS surface character lacking the presence of substantial amounts of alumosilicate is in good agreement with the TPD data showing also the excessive desorption of water.

The fact that Ru is so abundant on the surface is a further indication for the supported nature of the catalysts rather than for a possible intercalated species. The binding energy of 282.5 eV is high for Ru, an element with a very small chemical shift range. The difference in binding energy between Ru metal and RuO_2 is only 0.5 eV [11] indicating that the value found for the complex in free form (with the correct N : Ru ratio) identical as on the zeolite is determined by the molecular nature of the Ru and does not indicate a high oxidation state.

The binding energy for the Na in Na-A-Ru is the same as found in the literature [14] giving additional confidence in the internal consistency of the binding energy scale.

Table 1
XPS parameters of the catalyst precursors before thermal treatment. All positions in eV relate to the low energy peak of each signal. Abundances were calculated using the cross section tabulation of Briggs and Seah

	Ratio	Na-A-Ru			K-A-Ru		
		position	abundance	ratio	position	abundance	ratio
Na 1s	–	1071.4	1.3	–	1069.7	1.5	–
Si 2s	Si : Al	153.5	1.9	1.17	153.5	1.9	1.4
Al 2s	–	119.5	1.7	–	119.5	1.4	–
O 1s	O : Si	531.3	56.7	29.2	531.4	58.0	30.5
Ru 3d	Ru : Si	282.5	17.5	9.0	282.5	15.3	8.1
N 1s	N : Ru	400.0	19.6	1.12	400.0	20.6	1.3
Cl 2p	–	199.8	1.3	–	198.3	1.3	–
K 2p	K : Ru	–	–	–	293.8	0.1	0

Cycling a sample through activation, oxidation and re-reduction removes the water film and leaves the zeolite substrate rather unaffected. Its surface composition is comparable to the bulk elemental ratios (the O : Si ratio changes from 30.5 to 6.2). The elements chlorine and nitrogen are completely absent after activation due to desorption as NH_4Cl or HCl/N_2. The Na impurity in K-A-Ru also disappeared from the surface after activation indicating diffusion into the interior of the zeolite after the first heat treatment.

From table 2 it can be seen that both abundance and chemical state of Ru are affected by the redox treatments. Oxidation causes a drastic loss of surface Ru which is only partly recovered by re-reduction. The zeolite structure is unaffected but exhibits significant amounts of potassium and extra oxygen in the form of KOH on its surface. It is the process of oxidation which destroys the dispersion of the Ru. The possibility of forming volatile oxides such as RuO_3 is unlikely from inspection of the Ru–O phase diagram [15]. The observation of large crystalline Ru particles by XRD is strong evidence for agglomeration into particles significantly thicker than the information depth of XPS.

In the active state the zeolite oxide surface contains Ru in a form giving rise to a binding energy of 279.9 eV which is identical to that of bulk metal. The oxidation treatment causes an upshift of 1.4 eV which is far larger than expected for a "chemical" shift. Re-reduction finally results in Ru 3d 5/2 binding energy of 279.2 eV, a value which is likely to be an artefact as it is lower than the elemental reference energy. Both unusual shifts find an explanation if differential charging is assumed. The agglomeration reaction generates particles with little contact to the homogeneously charged zeolite substrate and of course without contact to the metallic sample holder. In this situation a different photoinduced charge can reside on the particles than on the substrate.

The evidence for differential charging was found by employing a variable addi-

Table 2

XPS parameters of a K-A-Ru sample after various thermal treatments in the XPS preparation chamber (see Experimental). The resolution parameter of the Ru 3d spin–orbit doublet is defined as the relative intensity ratio of the minimum between the two peaks and the maximum of the 5/2 peak. A value of 100 indicates complete overlap, 0 stands for complete separation

	Activated	Oxidised	Re-reduced	Bulk Ru
O/Si	6.20	7.30	6.00	–
Ru/Si	2.10	0.30	0.30	–
Si/Al	1.20	1.20	1.20	–
K/Ru	0.20	1.20	0.70	–
Ru (3d)	279.9	281.4	279.2	279.9
Si (2s)	153.5	153.5	153.5	–
K (2p)	293.8	293.8	293.8	
resolution (Ru 3d)	29	65	28	16

tional electrostatic field to the sample [16]. Using this method the charge difference between the particles and the substrate was found to be 0.7 eV for the re-reduced sample bringing the binding energy of the Ru back to 279.9 eV, the value for bulk metal. These "tubus" experiments further showed that there is only one species of Ru present, that no chemical reaction had occurred with the zeolite causing inhomogeneity (i.e. extraframework alumina) and that no carbon is present on the surface. This usual contamination element is difficult to analyse with Ru samples as the Ru 3d 1/2 peak exactly co-incides with the C 1s peak.

The different Ru 3d signals are presented in fig. 5. The effect of differential charging can be seen by the clear relative shifts between potassium 2p and ruthenium 3d. The intensity changes were discussed with fig. 4. Additional information about the chemical bonding of Ru can be extracted from the changes in lineshape. The Ru 3d 5/2 peak is in all spectra relatively sharp, its spin–orbit separation and the corresponding Ru 3d 3/2 peak differ, however, in their parameters. A superposition of different satellite structures over the main peaks explains the lineshapes observed in fig. 5. Spectra A and C are almost identical in their lineprofiles as crud-

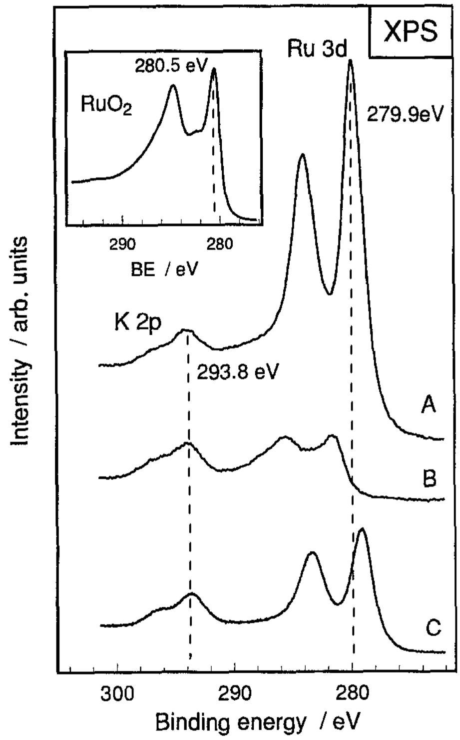

Fig. 5. Section of XPS data of K-Ru-A after various treatments in the in situ high pressure attachment of the spectrometer: (A) after activation and ammonia synthesis, (B) after full oxidation, (C) after re-reduction (for parameters see Experimental). The indicated line position for Ru is the reference for bulk metal, the K 2p position is characteristic of anhydrous KOH.

ely indicated by the resolution parameter in table 2 and are characteristic of metallic Ru. The particle size is larger than a few nanometers, a limit where pronounced lineprofile changes due to cluster electronic effects would be expected. An example of such size-modified lineshapes was found in the zeolite-Y-Ru samples discussed in the literature [11]. Precision analysis of the lineshapes before and after activation gave evidence that the precursor state may contain two slightly different Ru species (FWHM Ru 3d 5/2 2.47 eV) compatible with formal Ru^{3+} and Ru^{4+} in ruthenium red and one species (FWHM 1.81 eV) after activation. The linewidth is still 0.3 eV larger and the resolution parameter is worse than with a flat cleaned Ru metal sample, an effect attributable to the specimen surface irregularity.

Spectrum B in fig. 5 is strongly modified by satellite structures as reflected by the large resolution parameter (table 2) indicating the covalent bonding of Ru atoms to oxygen. This and the differential charging are clear indications for the bulk oxidation of the Ru. Comparison of spectrum B with the inset of the reference RuO_2 spectrum shows, however, that it is not the metallic conductor RuO_2 which was formed but an insulating variety. An amorphous structure or the suggested [17] formation of RuO_3 may be deduced from spectrum B in fig. 5.

A lineprofile analysis of the oxygen 1s data presented in fig. 6 allows to address

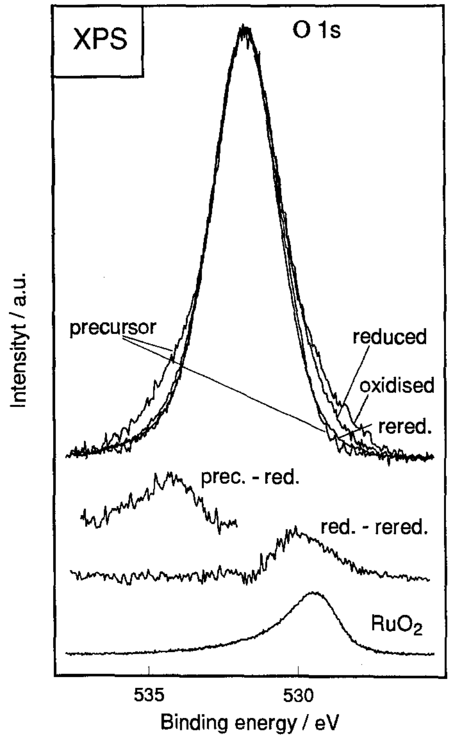

Fig. 6. Analysis of the oxygen 1s spectra. All peaks are normalised in intensity to allow comparison of the lineprofiles. A powder sample of characterised RuO_2 was used for the reference experiment.

the interaction of Ru with the zeolite. The main contribution of the signal is due to zeolitic or hydroxyl oxygen. The difference at high binding energy between the precursor and all other states of the catalyst is due to the loss of molecular water given off in the first heat treatment. The area under the difference peak relative to the total intensity is an indication about the surface sensitivity of XPS with the main contribution in this case originating from deep layers of the sample.

The asymmetries at low binding energies are rather similar for the activated and oxidised state and much reduced for the re-reduced state as can be seen from the difference plot in fig. 6. The low energy contribution arises from oxygen bonded to Ru as can be seen from the reference spectrum. In the activated state some Ru is bonded to oxygen from the zeolite providing anchor sites. After complete oxidation the RuO_2 O 1s peak is expected to increase in intensity. However, the order of magnitude loss in Ru surface area (see table 2) almost compensates for the increased number of oxygen atoms coordinated to each Ru atom in the oxide.

3.5. MORPHOLOGY

The morphological studies by TEM and SEM are summarized in fig. 7. Image A was obtained from K-A-Ru after in situ activation in the XPS instrument. The surface of the zeolite particle is covered with Ru particles of 2–10 nm in diameter. The same morphology is seen in image B taken from a sample of the microreactor after 750 h on stream. The fixation of the Ru withstands agglomeration for prolonged time as found already in the long term stability conversion test (fig. 2). If the catalyst is oxidised and re-reduced the dispersed metal is lost and a small number of well-developed large metal crystals can be observed in fig. 7C. Their size of about 20–60 nm agrees well with the XRD linewidth data. Finally, the SEM image D gives an impression of the cubic morphology of average zeolite particles with diameters of 2–4 μm.

4. Conclusion

Impregnation of Na-A or K-A zeolite with $Ru(NH_3)_6Cl_3$ in aqueous solution results in a purple precursor catalyst containing oligomeric Ru–oxo complexes with a mixture of amino and hydroxo/oxo ligands. Thermal treatment under defined conditions converts the precursor in a two-stage process (elimination of water/hydroxyl and of ammonia) into the active phase. Firmly bonded metal particles of a few nanometers size on the zeolite surface provide an efficient and stable ammonia synthesis catalyst. The system can store elemental nitrogen like the conventional iron catalyst. The K-A-Ru system works with potassium promotion at least at the interface metal–zeolite. The catalyst tolerates small amounts of oxygen poison. Under drastic oxidation conditions the metal–support bonds are irreversi-

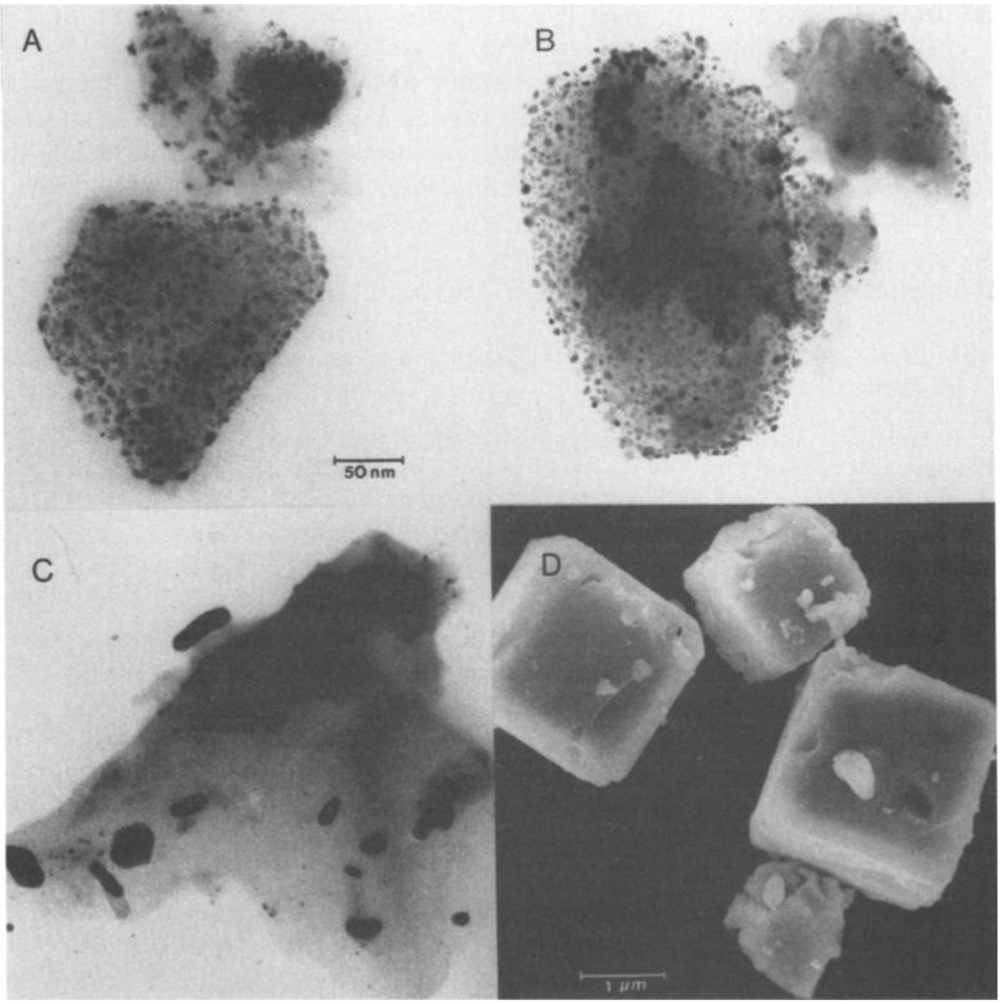

Fig. 7. Collection of TEM/SEM images of K-A-Ru samples after different treatments. (A) after in situ XPS activation, (B) after microreactor testing, (C) after full oxidation and re-reduction in the XPS, (D) SEM of sample A.

bly broken and bulk Ru oxides are formed. Re-reduction generates Ru metal particles not chemically fixed to the zeolite which sinter rapidly into large well-developed metal crystals rendering the catalyst inactive.

In contrast to a previously described Ru-Y zeolite system which was not long-term stable the present supported catalyst is stable. The insensitivity against small amounts of oxygen poison is an attractive feature of the catalyst which is a reference system for studies of intercalated Ru in zeolites. The importance of a well-designed preparation procedure yielding chemical anchoring of the metal to the zeolite is stressed.

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