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Application of Ru exchanged zeolite-Y in ammonia synthesis

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Na–Y zeolite was cation exchanged with $Ru(NH_3)_6Cl_3$ yielding at 25% exchange level a light-purple solid which was active in ammonia synthesis at atmospheric pressure. Pulse conversion experiments show that the catalyst stores nitrogen as it was observed with the conventional iron catalyst. At 810 K the conversion reached about 20% of the maximum conversion of the iron catalyst. The catalyst deactivated reversibly within 30 h due to agglomeration. The active species in the catalyst is most likely a cluster-like Ru metal particle prevented from sintering under the reducing conditions of catalysis by the zeolite framework.

Keywords: Ammonia synthesis; Ru–zeolite; metal clusters; conversion measurements

1. Introduction

A very large number of catalytic materials has been tested in the past [1] in order to overcome the kinetic limitations in efficient ammonia synthesis. Apart from iron, only ruthenium as active element has found some technical application in high pressure synthesis [2] with its high price preventing widespread use. Besides its favorable thermodynamic parameters for ammonia synthesis [3] it exhibits a low sensitivity against oxidative poisoning as can be seen from the formation enthalpies of the oxides (-824.8 kJ mol^{-1} for Fe and -305.0 kJ mol^{-1} for Ru). In order to test the hypothesis that oxygen poisoning is one major obstacle for low temperature ammonia synthesis a variety of supported Ru catalysts were synthesised and tested. First characterisation results were

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published recently [4], the present contribution focuses on a more complete characterisation and on the catalytic performance of the system Na–Y zeolite ion exchanged with Ru.

Ru exchanged zeolite Y was prepared and characterised earlier [5] in applications for CO hydrogenation. Recently, a catalyst prepared by addition of Ru to the hydrothermal synthesis mix of zeolite A was described and tested with hydrogenation and hydrogenolysis reactions [6]. The nominally similar Na–Ru–Y zeolites used in hydrogenation experiments and prepared for this study exhibit very different stabilities against segregation of the metal to the external surface. XPS in situ studies on both systems [4,5] reveal a high stability of our samples against reductive agglomeration up to 800 K which was very prominent with the previous material. In the light of recent understanding of the processes associated with metal cluster formation in zeolites [7,8] these differences may be traced back to different impregnation/calcination procedures leading to a location of the Ru in the supercages in our materials and in the sodalite cages in the previous samples.

2. Experimental

2.1. CATALYST SYNTHESIS

Na–Y powder (≈ 5 μm size) was cation exchanged in 0.05 molar aqueous $Ru(NH_3)_6Cl_3$ solution at 335 K for 48 h using a stoichiometry for the exchangeable cations of 25%. After washing and drying at 373 K in vacuo a light-purple powder is obtained containing 2.9 wt% Ru according to XRF analysis. The X-ray powder diffraction pattern (Co K_α radiation, transmission geometry) was almost unchanged with respect to lattice parameter and intensity ratios compared to the starting pattern. The nitrogen BET surface (gas flow method, Quantasorb instrument) of the material was reduced from 830 to 41 $m^2\ g^{-1}$. Surface analysis by XPS yielded a Si : Al ratio of 2.1 (in the nominal material 2.43) unchanged by cation exchange and a Ru : Si ratio of 21.3×10^{-3} compared to the bulk ratio of 36.7×10^{-3}. For a reproducible synthesis of the material the purity of the starting complex monitored by UV-Vis, IR spectroscopy and elemental analysis was found to be vital. Other Ru starting compounds (Ru II complexes or $RuCl_3$) gave either no reproducible loading or completely inactive catalysts.

2.2. CATALYTIC TESTING

The measurements were carried out in a microreactor setup used previously in experiments with the conventional iron catalyst [9]. Typically 125 mg loose powder were applied yielding a catalyst bed of 20 mm height. The catalysts were either activated in situ or subjected to a reductive calcination in hydrogen at 673 K for 80 h. After this treatment all catalysts showed a dark colour but neither the BET surface area (41 m^2 g^{-1}) nor the XRD pattern nor the XPS surface composition (Ru : Si ratio 20.7×10^{-3}) showed a significant change. The conversion measurements described here were done at a flow of 2.37 ℓ h^{-1} $N_2 : H_2$ 1 : 3 mixture at atmospheric pressure.

The active metal surface area was determined from a hydrogen uptake measurement in a static gas adsorption system after pretreating the sample with hydrogen at 673 K followed by evacuation at 673 K for 30 min. Adsorption was determined at 305 K with 500 mbar hydrogen. This method was established using Ru powder with the data of nitrogen BET and hydrogen uptake measurements being finally in coincidence. Saturation of the catalyst samples took up to 2 h yielding an active surface area of 1.4 m^2 g^{-1}. For the turnover number calculations a surface area of 817 pm^2 [10] for a Ru atom was assumed.

Photoemission data were recorded with loose powders analysed in the as-received state and after in situ hydrogenation and oxidation at 673 K and 100 mbar for 3 h each. Spectra were recorded with an analyser pass energy of 100 eV using Al K_α radiation. Charging was corrected using Si 2s at 154.0 eV; this value was established in a flood gun experiment which chemically reduces the Ru present with a sample of Na–Y zeolite [4].

3. Results and discussion

The results will be discussed using data from a sample US24-1 which is representative of a total of 12 catalyst preparations. The XPS surface analysis of the starting material in at% was Na 5.9%, Ru 0.5%, C 4.6%, O 55.0, Si 23.0% Al 11.0% [4].

3.1. CONVERSION MEASUREMENTS

Conversion data as function of temperature are shown for three catalyst preparations in fig. 1. Modification of the synthesis procedures increased the high temperature yields significantly. The thermodynamically controlled branch of the curve was not reached at steady state conditions due to deactivation at the high absolute temperatures required. The best conversions reached about 20% of the value observed with the commercial iron based catalysts (see inset of fig. 1 and ref. [9]). The temperature of maximum conversion was strongly dependent on the gas flow with a lower value at low gas flows and could not be reduced to a constant value while reducing the space velocity to the minimum possible in the present setup: all catalytic activities are thus unfavourable approximations to the optimum performance possible with Ru as catalyst material.

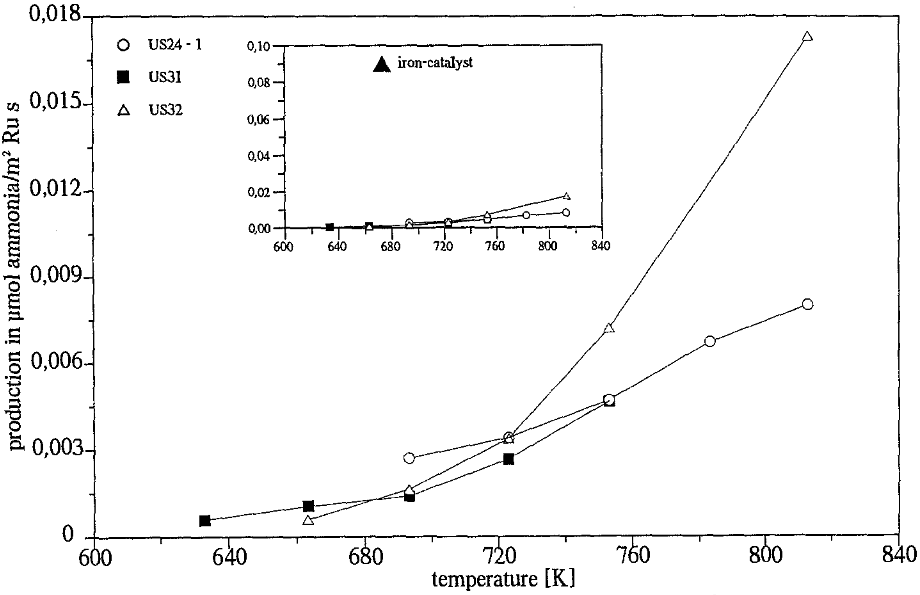

Fig. 1. Conversion (in µmol NH_3 m^{-2} s^{-1}) versus temperature characteristics of three catalyst samples. The inset (ordinate reduced by a factor of 10) indicates the relation of the present data to the performance of the standard Haldor Topsøe KM1 catalyst measured under similar conditions. The active surface areas determined with CO chemisorption (Fe) and H_2 chemisorption (Ru) were used for the comparison.

Stability tests showed that the turnover at 693 K stayed constant for up to 70 h at a level of 18×10^{-5} (s^{-1}). At the level of maximum conversion (813 K, 54×10^{-5} (s^{-1})) the turnover dropped within 30 h back to the level of 693 K. This long-term deactivation was found to be reversible by a controlled oxidative treatment in nitrogen gas over 24 h. Alternatively, cooling in synthesis gas mixture followed by a short exposure to air and re-activation also restored the initial catalytic activity and improved the time constant of deactivation. Short temperature shocks of 50 K helped to increase the maximum conversion with no influence on the deactivation process.

All these observations point to a stable form of the active catalysts up to 800 K and a reversible agglomeration of the Ru at higher temperatures. This was evidenced using transmission electron microscopy showing no particulate contrast with the as-received or as-calcined samples. Agglomeration was observed, however, after deactivation in ammonia synthesis leading to the hexagonal platelets displayed in fig. 2. Exposing the catalyst for 60 h to pure hydrogen at 813 K led to a detectable formation of crystallites of Ru metal. In fig. 3 the transmission XRD trace of the hydrogen treated sample is shown exhibiting no signs of deterioration of the zeolite matrix. In the inset the difference diffractogram to the calcined sample US 24 indicates, however, clearly the formation of crystallites of Ru metal. Particle sizes in TEM and XRD of ≈ 10–30 nm

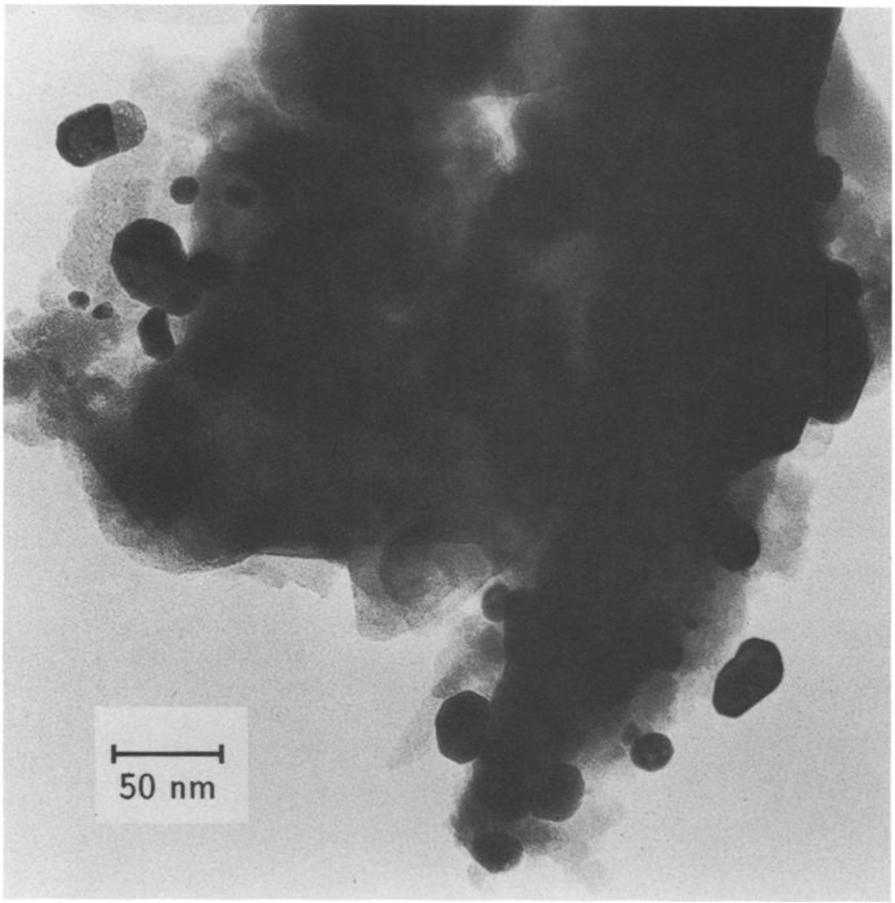

Fig. 2. TEM image of US 24 after deactivation in ammonia synthesis at 810 K. Segregated Ru metal (electron diffraction) particles are clearly visible.

agree so that there is little doubt that as result of extensive reductive high temperature treatment the Ru segregates out of the zeolite matrix and agglomerates to metal crystallites. Close inspection of the contrast within the Ru crystals in fig. 2 reveals a very large number of defects associated with the crystals giving rise to the potential reactivity in re-dispersion under non-reducing conditions.

After ≈ 800 h on stream the steady-state turnover at 663 K had increased to $\approx 6.0 \times 10^{-4}$ (s^{-1}). At this performance a non-stationary conversion experiment was performed similar to those described in ref. [9]. The result is displayed in fig. 4. At zero time the gas feed was changed to pure nitrogen and the conversion drops to a small level given by the thermal decomposition of acid site

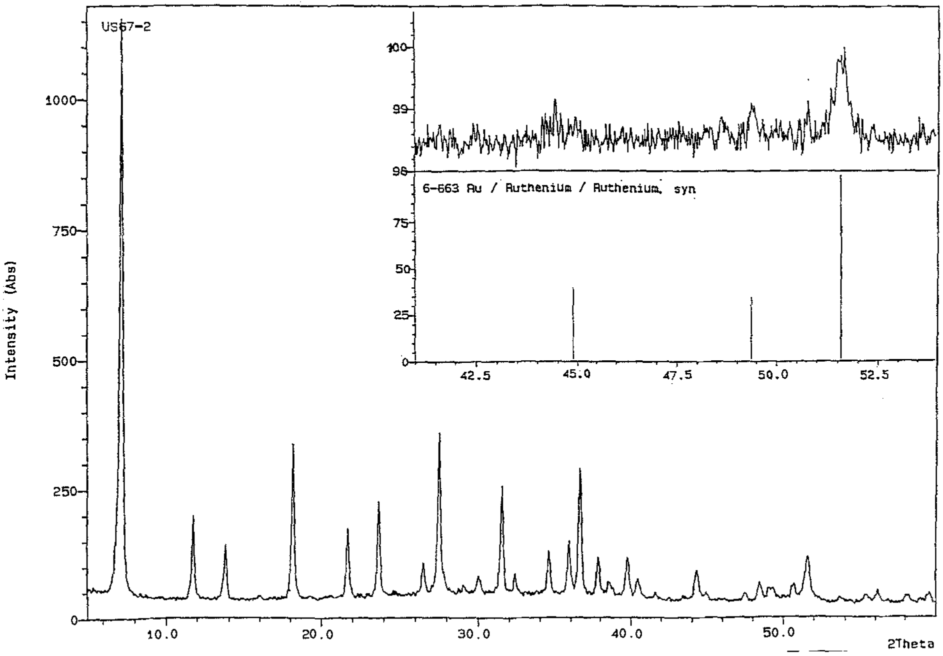

Fig. 3. XRD transmission diffraction pattern (Co K_α radiation) of US 24 after treatment with hydrogen at 813 K for 60 h. The inset shows a section of the difference diffractogram between the calcined sample and the hydrogen treated catalyst with the JCPDS bar diagram identifying the peaks as Ru metal.

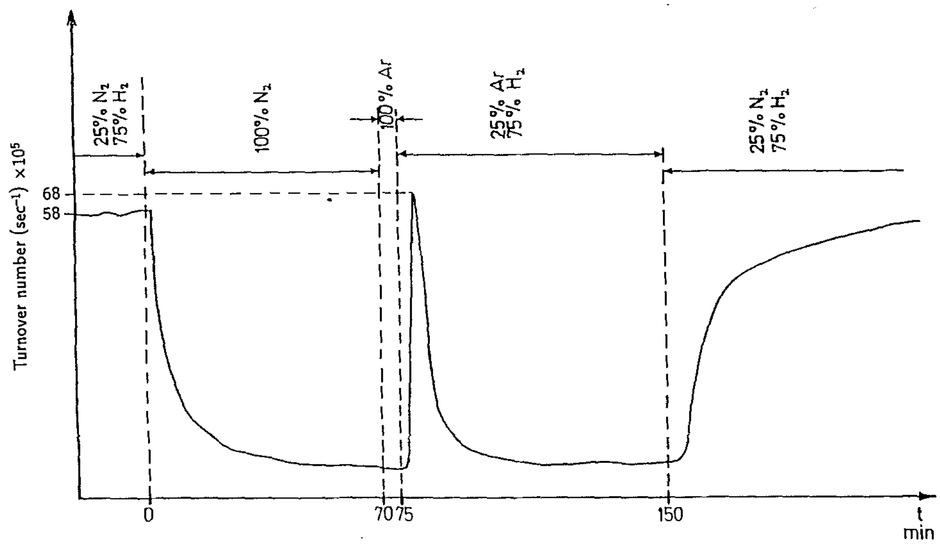

Fig. 4. Pulse conversion experiment with US 24 after prolonged time on stream. The time scale is relative to the beginning of the experiment.

complexes and diffusion out of the zeolite. This process occurs also with totally unreactive Ar indicating that the catalyst does not store hydrogen. After 75 min the feed is changed to an Ar : H_2 mix and the formation of ammonia from stored nitrogen is observed. The height of the ammonia pulse depends on the time allowed for saturation of the catalyst with nitrogen; exposures of 20 to 250 min led to pulses ranging from 4 to 188 ppm of ammonia. At time 150 min (fig. 4) the feed is restored to its initial composition and complete recovery of the turnover occurs in about 60 min. The catalyst behaves similarly as the conventional iron catalyst but the responses are with $\approx$ 10 min significantly slower than with the iron catalyst (2 min) indicating that gas diffusion processes within the zeolite pore system play an important role. This is further substantiated by the fact that the make-up gas in the pulse experiments influences the pulse yield with helium extracting less than half of ammonia than argon. The final slow recovery in fig. 4 may be a consequence of both the recharging of the storage support and of short time deactivation of the active Ru by gas impurities such as O_2 and CO brought into the system by the gas switching procedures.

3.2. NATURE OF THE ACTIVE MATERIAL

The light-purple material is believed to be a partly ion exchanged zeolite with the Ru located inside the micropore system. The very high selectivity of the process (no reaction with Ru II salts, precipitation with Ru III chloride) and the fact that the Ru was re-exchanged as $Ru[(NH_3)_5OH]^{2+}$ complex identified by its UV absorption at 299 nm [11] after addition of KCl solution support this picture as it also follows from XPS surface analysis and TEM observations. Bulk elemental analysis showed that both nitrogen and chlorine content of the light-purple compound were in agreement with the molecular identity of the starting complex. Analysis of the exchange solution for the alkali ion revealed 85 at% of the abundance expected for ion exchange with Ru with the 15% difference being due to the presence of other exchangeable cations.

Calcination liberates the molecular ligands as ammonium chloride, ammonia and nitrogen/hydrogen, a process which is facilitated by additional hydrogen from the gas phase. This can be seen from the NH_3 TPD traces in fig. 5 which were recorded with an IMR-MS mass spectrometer [12] under identical conditions as those applied for activation in the microreactor.

During these experiments it was observed that hydrogen gas led to an evolution of molecular oxygen presumably stored from air in the pores of the zeolite. Its partial pressure fell abruptly to zero at the temperature of maximum NH_3 evolution supporting the hypothesis of an intermediate Ru-oxide in the calcination stage of the catalyst [8]. The Ru content is affected neither in the bulk (XRF) nor at the surface (XPS). At this stage the catalyst consists of Ru metal clusters entrapped in the zeolite framework and protons as charge counterions for the lost alkali. A high resolution scan by XPS through the Ru 3d

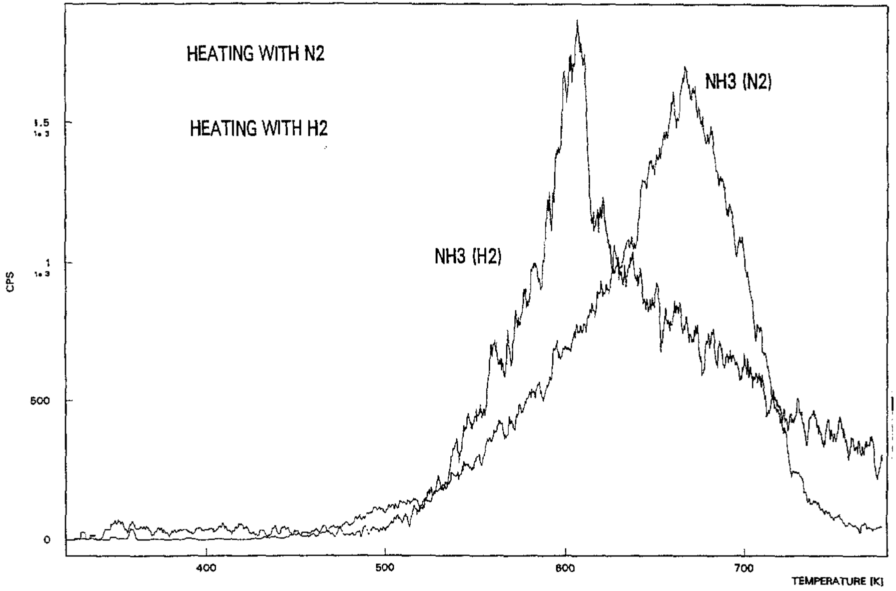

Fig. 5. IMR-MS temperature programmed reaction profiles of US 24 after ion exchange recorded with either reducing or inert carrier gas.

region of the catalyst after in situ operation in the spectrometer is compared in fig. 6 with the spectra of Ru metal and of RuO_2 shifted by 0.5 eV to lower binding energy in order to bring the 3d 5/2 emissions into coincidence. The line position of the Ru in the catalyst agrees with 279.8 eV very well with the position for bulk Ru metal of 280.0 eV. RuO_2 exhibits only a shift of 0.5 eV relative to the metal, but nevertheless an oxidic nature of the calcined catalyst can be excluded. This is substantiated in the line profiles of fig. 6 showing similar main transition profiles but significantly different satellite structures at higher binding energies. The final state effects of the catalyst Ru are dissimilar to those of RuO_2 but also to those of bulk Ru metal (clearer separation of the 3/2 to 5/2 emissions, smaller linewidth). Small particles of a metal with cluster dimensions do show spectra intermediate between those of bulk metal and free atom due to their incompletely formed conduction band. The inset in fig. 6 compares the Ru 3d 5/2 peaks of the sample in situ operated in the microreactor after transfer and after subsequent in situ hydrogen reduction. After deactivation the Ru is present in such large particles that no extra satellites and large shifts occur upon oxidation in air, i.e. the Ru was transformed into normal RuO_2 which could be easily re-reduced to the metallic state. Oxidation of the still active Ru led to very pronounced final state effects indicative of the cluster nature of the entrapped Ru [4].

This picture of entrapped metal particles within the zeolite is consistent with the reduction in its surface area. A thin surface film of metal susceptible to

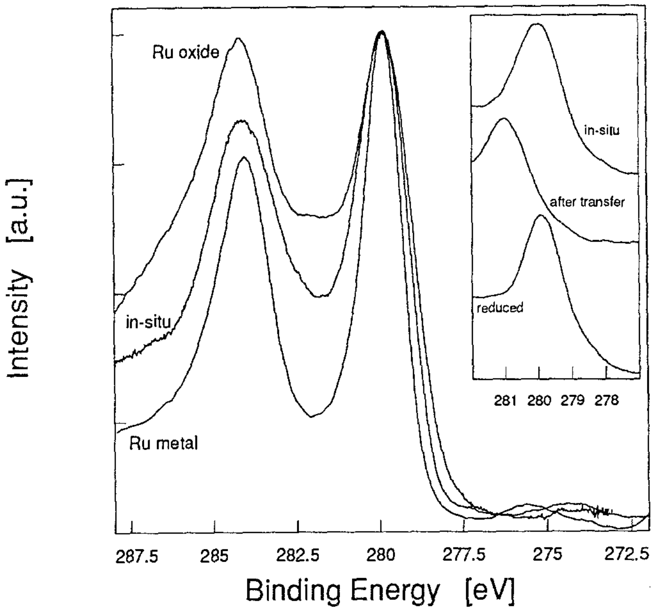

Fig. 6. XPS high resolution scans through the Ru 3d region of the US 24 catalyst after in situ ammonia synthesis at atmospheric pressure, with Ru metal and RuO_2 as reference compounds. The spectrum of RuO_2 was shifted by 0.5 eV to bring all maxima of the 3d 5/2 transition into co-incidence. The absence of carbon impurities which overlap with the Ru 3d peaks was checked with the C KVV Auger spectrum. The inset shows reoxidation (0.9 eV shift) of the in the microreactor deactivated material upon transfer in air.

agglomeration is excluded from the unchanged XPS composition after calcination or ammonia synthesis and from the hydrogen titration value. Large metal particles possibly also consistent with the XPS data and hydrogen adsorption occur only after deactivation and only then their existence can be shown by XRD and TEM.

The location of the Ru metal clusters activating molecular nitrogen inside the zeolite framework can also be deduced from the much enlarged time constants of the "in situ" pulse turnover experiment and from the observation that the conversion data are affected so severely by gas transport kinetics. Access of the gas molecules to the inner surface is only possible due to the low degree of cation exchange allowing sufficient pores to stay empty from Ru.

The picture of the active catalyst is thus a distribution of "grape-type" [5] Ru clusters within some supercages inside the zeolite. The observed variation in BET area of different catalyst preparations indicates the distribution of these pore blocking clusters within a zeolite crystal being ring-shaped with a radius close to the particle radius for low surface area preparations such as US 24, whereas a high surface area will result from a statistical cluster distribution.

The clusters are of zerovalent Ru which can activate and store nitrogen similar to the situation with the iron catalyst.

In order to fully exploit the potential of the Ru–zeolite catalyst system the gas transport limitations must be removed which will be attempted by preparative measures to optimise the Ru distribution inside the zeolite.

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