



Comparison of oxidised polycrystalline copper foil with small deposited copper clusters on their behavior in the ammonia oxidation: an investigation by means of in situ NEXAFS spectroscopy in the soft X-ray range

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Abstract

The oxidation of ammonia to nitrogen or nitric oxide, respectively, was investigated using on the one hand a polycrystalline copper foil and on the other hand deposited copper clusters prepared with the inert gas aggregation technique. The behavior in the ammonia oxidation of both model catalysts was studied using in situ near edge X-ray absorption fine structure (NEXAFS) spectroscopy in the soft X-ray range and mass spectrometry. It is shown that the copper foil reacts in a similar way as the copper clusters. Differences appear only with respect to the reaction temperature required, which is lowered for the cluster sample. It can be concluded that results obtained in experiments with polycrystalline copper foil are exemplary for and can be transferred to supported copper catalyst consisting of small copper particles.

Keywords: catalytic oxidation of ammonia, polycrystalline copper foil, copper cluster, in situ NEXAFS, copper (I) nitride

Introduction

The partial oxidation of ammonia to nitrogen and water is a widely used process for the ammonia slipstream treatment after the DeNO_x-SCR [1] or for purification of reformates in fuel-cell applications [2]. Recent investigations showed that copper can be used as a catalyst for this oxidation [1-3]. We studied the ammonia oxidation over copper with in situ NEXAFS spectroscopy and were able to show that the catalytically active surface for the partial oxidation to nitrogen is copper (I) oxide whereas copper (II) oxide catalyzes the total oxidation to nitric oxide [4]. In contrast to our investigations with polycrystalline copper foil as model catalyst, the catalysts used in industrial applications are oxide or zeolite supported copper particles and clusters, respectively. Therefore, the question arises whether the results obtained with copper foil are exemplary also for supported catalysts. With regard to many studies of the reaction behavior of clusters or small particles in general, the clusters are expected to react at

some lower temperature. Furthermore, it remains to be shown that small copper particles react in the same way and to the same products than extended copper surfaces.

To answer these questions, we prepared small copper cluster with an average diameter of 2.8 nm by means of the inert gas aggregation technique on a gold grid covered with an amorphous carbon film, which is typically used in TEM microscopy. These copper cluster had to undergo the same reaction conditions as the copper foil we investigated before, except the temperature, which was increased very carefully from room temperature to 470 K while the NEXAFS spectra were recorded in a flowthrough reactor. Before and after the reaction TEM images were taken to verify the morphology of the clusters.

Experimental

All experiments were carried out in a system consisting of two UHV chambers. One is used as reaction chamber and is

separated from the second by a 100 nm silicon nitride X-ray window providing a 4 mm aperture and withstanding a pressure difference of at least 100 mbar. The second chamber with a base pressure of $p < 5 \times 10^{-9}$ mbar was connected to the undulator beamline UE56/2-PGM1 [5], at BESSY II, the Berlin electron storage ring for synchrotron radiation. The mixture of the reaction gases is controlled by calibrated mass flow controllers, and the pressure is regulated with a valve in the outlet stream. The gas phase right above the sample is sucked off via a capillary (i.d. 1 mm) and analyzed in a mass spectrometer. Thus a continuous monitoring of the gas phase is provided and gives the possibility to associate the actual gas phase composition with the NEXAFS spectra. Therefore, a correlation of the reaction products and the conversion, respectively, with the surface state of the catalyst is feasible. The NEXAFS spectra are recorded with a detector device operating in total-electron-yield-mode (TEY) and is described in detail in refs. [6-9]. The main feature of this detector device is the simultaneous but independent recording of the electrons emitted only from the gas phase and a mixed signal representing electrons from both the surface and the gas phase. After subtracting the pure gas phase from the mixed spectrum one obtains the desired NEXAFS spectra which show resonances only from the sample [4].

The cluster sample is prepared using the gas aggregation technique [10,11], which allows to produce metal clusters in the large size range (10-30 nm) as well as in the intermediate size range (1-10 nm). The experimental setup, which was used here, is described in detail elsewhere [12,13]. In this case the copper clusters were generated with a mean size diameter of 2.8 nm. Copper (Alfa, 99.99%) was evaporated from a Knudsen cell by direct heating into an argon gas atmosphere. The copper vapour was efficiently cooled by collisions with gas atoms by means of a liquid nitrogen cooling-trap. In regions of sufficiently high supersaturation a homogeneous nucleation occurs. This aggregation process is interrupted by a helium-cooled cryo-pump where most of the argon gas was condensed. An aperture on the axis of this pump allows the production of a collimated cluster beam. The clusters were then deposited on a Au-grid covered with an amorphous carbon film usually used in electron microscopy. After the deposition of the clusters the particles were exposed to air for two hours and afterward their distribution was investigated with an electron microscope (Philips CM200 FEG, max. resolution 0.18 nm). In order to control if the reaction conditions had caused morphological changes like sintering, the sample was re-investigated by means of TEM after the reaction.

The copper foil (99.99+%, Goodfellow), which has a size of ca. 25×13 mm, was prepared to a Cu_2O surface by complete oxidation to CuO at 670 K in 1.0 mbar O_2 , and following annealing in UHV to 720 K. After this procedure the NEXAFS spectrum at the Cu L_3 -edge showed only resonances of copper (I) oxide [14].

The reaction conditions used for both, the copper foil and cluster experiments, was a mixture of ammonia (99.98%, Linde, flow of 0.38 Sml/min.) with 4.5 Sml/min. of oxygen

(99.9990%, Linde) providing a ratio of $\text{NH}_3:\text{O}_2 = 1:12$. The overall pressure used in the investigations presented here was $p_{\text{abs}} = 1.2$ mbar, and the temperature was increased stepwise from 300 K up to 670 K (foil) or 470 K (cluster), respectively.

Results

Copper foil

We recently published results of the pressure dependence of the ammonia oxidation reaction obtained with copper foil as model catalyst which was preoxidized to copper (II) oxide as initial state [4]. It was shown that a temperature of at least 570 K is needed to ignite the reaction and an increase to 670 K doubles the ammonia conversion. However, at an absolute pressure of $p_{\text{abs}} = 0.4$ mbar an immediate reduction to Cu_2O occurred, followed by a deactivation within one hour due to the formation of copper (I) nitride. In contrast, at $p_{\text{abs}} = 1.2$ mbar the reaction remained steady for at least two hours, but a very slow shift in the distribution of the products toward less nitric oxide and increasing nitrogen occurred. Simultaneously, the catalyst surface was reduced from pure CuO to a mixture of CuO and Cu_2O . At an intermediate pressure of $p_{\text{abs}} = 0.8$ mbar a slow but steady change in the main product gas from nitric oxide to nitrogen was visible with a simultaneous modification of the catalyst surface from CuO to Cu_2O . Thus, a structure-function-relation was established, pointing out that copper (I) oxide catalyzes the desired partial oxidation of ammonia to nitrogen, whereas the total oxidation to nitric oxide is catalyzed by copper (II) oxide.

To sustain this, an additional experiment was carried out at an absolute pressure of $p_{\text{abs}} = 1.2$ mbar, starting with copper (I) oxide as initial state of the copper foil. The mass spectrometer data of this reaction are presented in Fig. 1:

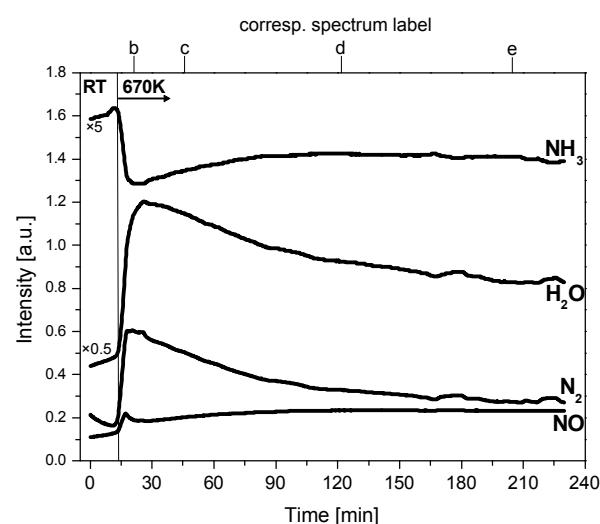


Fig. 1: Mass spectra of NH_3 , NO , H_2O , and N_2 of the reaction at $p_{\text{abs}} = 1.2$ mbar, $\text{NH}_3:\text{O}_2 = 1:12$, copper foil

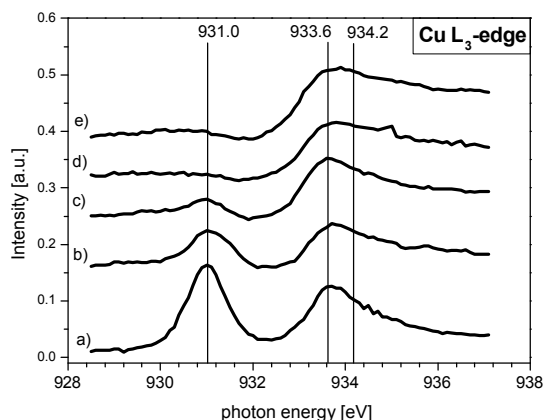


Fig. 2: NEXAFS spectra at the Cu L₃-edge from the reaction of the copper foil at $p_{\text{abs}} = 1.2$ mbar, $\text{NH}_3:\text{O}_2 = 1:12$ at a) room temperature, b) after 5 min. at 670 K, c) after 30 min. at 670 K, d) after 110 min. at 670 K, and e) 190 min. at 670 K.

After increasing the temperature up to 670 K the ammonia oxidation occurs with a maximum conversion of $\text{XNH}_3 = 41.9\%$ after 5 minutes time on stream, which is in good agreement with the results obtained earlier [4]. Like expected by the previous results, the selectivity to nitrogen is high ($\text{SN}_2 = 76.9\%$) at the beginning of the reaction. Within 3 hours the conversion of the ammonia drops to $\text{XNH}_3 = 18.6\%$ and the selectivity to nitrogen is decreased to almost 50%. The NEXAFS spectra of the copper L₃-edge (shown in Fig. 2) reveal the reason for this deactivation: the formation of copper (I) nitride, which is identified by the resonance at 934.2 eV in contrast to the initial copper (I) oxide with its resonance at 933.6 eV [14]. The reason for the remaining activity is the co-existence of copper oxide patches with the nitrated surface as indicated by the broadened resonance structure for the nitride, which is not induced by the spectral resolution of the experiment.

In contrast to a pressure of $p_{\text{abs}} = 0.4$ mbar [4], it takes several hours and thus very much longer to form the copper (I) nitride. Moreover, only a partial deactivation ending in a reduced steady state activity of the copper catalyst takes place at an absolute pressure of $p_{\text{abs}} = 1.2$ mbar, providing a larger excess of active oxygen required to prevent irreversible, complete nitridation.

Copper clusters

The NEXAFS spectra of the copper L₃-edge from the cluster sample in Fig. 3 show that the initial state of the cluster was a mixture of copper (I) oxide (933.6 eV) and copper (II) oxide (931.0 eV). Since a fresh mounted copper foil never exhibited any CuO but only Cu₂O, this gives evidence for the high reactivity of these small particles even at room temperature. The cluster sample was heated only up to 470 K in the reaction atmosphere. This temperature is high enough to cause a reduction of the copper (II) oxide to Cu₂O as can easily be seen by the disappearance of the CuO-

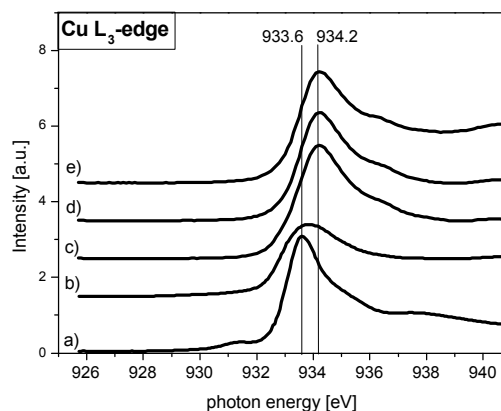


Fig. 3: NEXAFS spectra at the Cu L₃-edge from the reaction of the copper cluster at $p_{\text{abs}} = 1.2$ mbar, $\text{NH}_3:\text{O}_2 = 1:12$ at a) room temperature, b) after 5 min. at 370 K, c) after 5 min. at 420 K, d) after 30 min. at 420 K, and e) 5 min. at 470 K.

resonance at 931.0 eV. The formation of copper (I) nitride is visible by the obvious broadening of the resonance if compared to spectrum (a), which is caused by the superposition of a large contribution from Cu₂O with a small contribution from Cu₃N, resulting in the reverse situation as discussed with figure 2. The spectral resolution is reduced here compared to the experiments with copper foil due to the extremely small amount of the sample (about 100 nmol copper). The spectral behaviour qualitatively similar to that discussed with the copper foil gives evidence that a reaction with the ammonia-oxygen-mixture occurred, and the well known formation of copper (I) nitride took place. The mass spectrometer data give an additional hint on the catalytic activity of copper clusters in the ammonia oxidation as shown in Fig.4. There occurs small changes of the volume flow from the reaction cell into the differentially pumped mass spectrometer due to varying gas temperature and condensation problems that might induces ion current changes although no reaction took place. The ion current signals were normalised on the signal of $m/e=15$. The masses $m/e=14$, $m/e=15$ and $m/e=17$ represent fragments of ammonia, therefore the normalised $m/e=17$ signal is a straight line. The resulting signal for $m/e=14$ clearly shows distinguishable peaks at 44 min (370 K) and at 81 min (420 K) that can be caused only by nitrogen containing species different than ammonia. Since a peak for the $m/e=28$ coincides with the peak in the signal for $m/e=14$ it can be concluded that this signal is not an artefact (ensured by the normalisation procedure) and can be attributed unambiguously to the production of N₂. A peak in the ion current of NO (24min) is observed additionally to the peak for N₂ at 420 K. The yield of NO and N₂ shows peaks which occur not immediately after temperature increasing. The unsatisfying thermal contact between the TEM grids with the deposited cluster on it and the heating stage might be the reason for the delay.

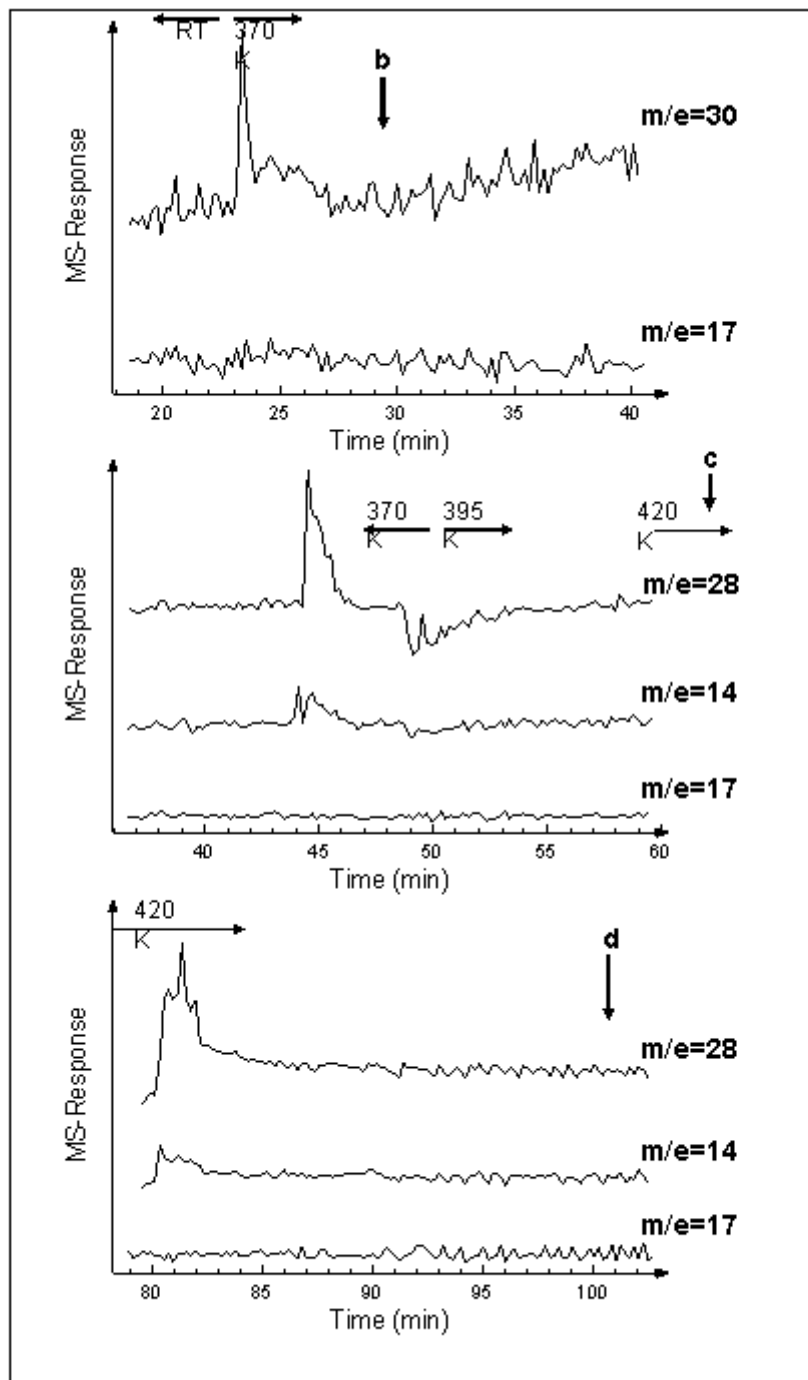


Fig.4: Mass spectrometer signal of NO($m/e=30$) and N_2 ($m/e=28,14$) normalised on the ion current of ammonia ($m/e=15$) are plotted as a function of time. The masses $m/e=14$, $m/e=15$ and $m/e=17$ represent fragments of ammonia. The straight line of $m/e=17$ after normalisation demonstrates the successful remove of artefacts. Since the peaks of $m/e=14$ at 44 min (370 K) and 81 min (420 K) coincide with peaks in $m/e=28$ it can be concluded, that the signal is due to the formation of nitrogen. The temperature of the catalyst is indicated in the Figure. The time scale is given relatively to the detection moment of NEXAFS spectrum a) in Fig. 3. The detection moment of NEXAFS spectra b,c and d (Fig. 3) is indicated by arrows in the plot.

The TEM image of the copper cluster sample before the reaction is presented in Fig.5. The clusters with a mean size of 2.8 nm are distributed randomly over the support. The TEM image after the reaction (Fig. 6) and the comparison of size distribution of the clusters before and after reaction in Fig. 7 reveal, that the average diameter of a large fraction of

the clusters had increased, indicating a partial sintering of the weakly supported clusters. But, due to the fact that no film formation by spreading of the clusters occurred, it can be pointed out that evidently the clusters have reacted. Moreover, the contrast of the clusters after reaction is slurred, indicating a loss of internal ordering being a conse-

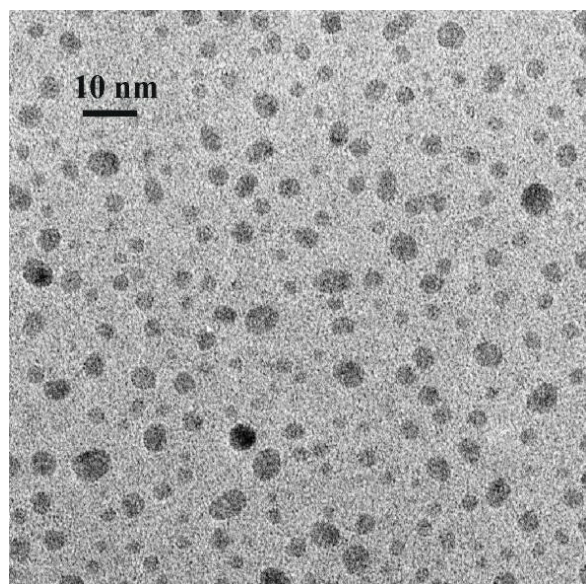


Fig.5: TEM image (ca. 110 nm × 110 nm) of the copper cluster sample before the reaction. Average particle diameter: 2.8 nm.

quence of the spectroscopically observed chemical transformation.

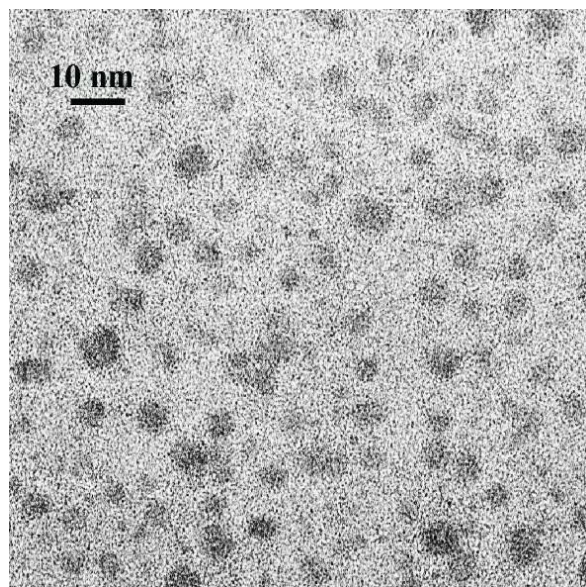


Fig.6: TEM image (ca. 110 nm × 110 nm) of the copper cluster sample after the reaction. Average particle diameter: 4.45 nm.

Discussion

The results obtained with a copper foil as model catalyst, which are presented here and in Ref. [4], show, that a deactivation of the partial oxidation activity due to formation of copper (I) nitride can not be avoided at all pressures from 0.4 mbar up to 1.2 mbar after the sample has reached a maximum abundance of Cu₂O. The nitride formation as a possible reaction of copper oxides with ammonia was found first by Schroetter in 1841 [15] but could also be seen in

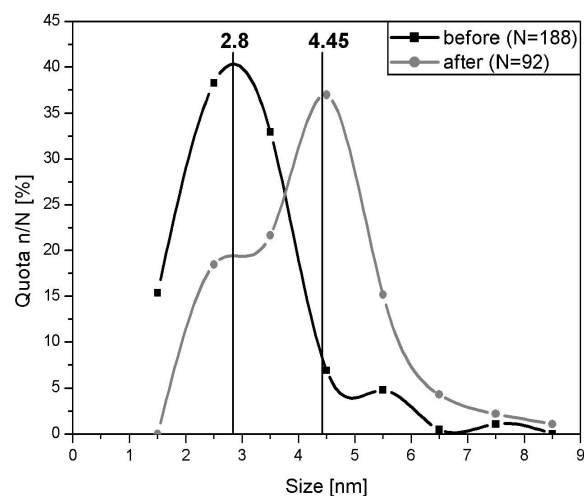


Fig.7: Size distribution of the copper clusters before (■, black) and after (●, grey) the reaction.

recent UHV studies of copper single crystals [16,17]. It can be concluded that the clusters reacted with the ammonia as well because of the increasing formation of Cu₃N which is visible in the NEXAFS spectra of the copper cluster sample (Fig. 3, spectra c → e). The formation of copper (I) nitride gives evidence that the ammonia oxidation occurred at these clusters since there is no other possibility to form Cu₃N in this atmosphere. Additionally, the production of NO and N₂ and therefore the catalytic activity of the copper clusters could be demonstrated by the normalisation of the related ion current on the ion current of ammonia (m/e=15). Peaks in the ion current of m/e=30 and m/e=28 indicate at least the temporary formation of NO and N₂ by the catalytic oxidation of ammonia over copper cluster. The formation of N₂ in the gas phase coincides with the formation of Cu₃N on the catalyst's surface. The decreasing abundance of CuO on the surface (Fig. 4, spectra a → b) is coincided by the formation of NO. Therefore, the same structure-function-relation as established for the copper foil can be assumed for the interaction of the ammonia/oxygen mixture with the copper clusters. Even if the TEM images show that the clusters had slightly sintered, the particular cluster topology remained and no spreading and film formation occurred. Therefore, the NEXAFS spectra in Fig. 3 were evidently obtained from the clusters, which reacted with the ammonia.

Conclusions

We present here results received with copper foil as a model catalyst and compare them with such obtained with deposited copper clusters. Since a copper (I) nitride formation occurred in both cases, it can be concluded that the foil reacts in a similar way and to the same products as small particles or clusters, except for the reaction temperature which is much lower in the latter case. The observed peaks in the ion current of NO and N₂ gives a hint on the catalytic activity of copper clusters in the ammonia oxidation. It can be

assumed that the experiments and results obtained with copper foil as model catalyst in the ammonia oxidation are exemplary for the reaction behaviour of copper clusters or small particles. The results of an in situ investigation of so called nano-particles under the mentioned reaction conditions (1.2 mbar, 470 K) presented in this publication can be regarded as an important step in the investigation of small particles and their reaction behaviour, scientifically as well

as methodically.

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