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Review

Evolution, achievements, and perspectives of the TAP technique

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Abstract

This manuscript concisely reviews the significance of the temporal analysis of products (TAP) technique in catalysis research from its introduction to the scientific community in the late 1980s. Evolutionary aspects of this time-resolved transient pulse method are presented, highlighting its relevance for elucidation of mechanistic and kinetic aspects of adsorption, diffusion, and reaction in gas–solid systems. The high-temperature ammonia oxidation over noble metal catalysts is used to underline key advantages of the TAP reactor in mechanistic studies, narrowing the often-encountered pressure and materials gaps between techniques operating at ambient pressure and in ultra-high vacuum. Perspectives to further enhance the capabilities of this technique are briefly put forward.

Keywords: Temporal analysis of products; Transient methods; Heterogeneous catalysis; Gas–solid reaction; Mechanism; Kinetics

Contents

1. Approaches to mechanistic studies: locating the TAP reactor

Heterogeneous catalysis is the basis for the majority of processes in the chemical industry. However, there is still a high demand for more efficient, environmental benign production technologies that guarantee optimal exploitation of feedstocks and shorten the time-to-market of new products. Catalyst development in industry is still based on time-consuming trial-and-error approaches, often leading to incremental improvements in the process. This can largely be attributed to a lack of in-depth understanding of reaction mechanisms and kinetics, and of correlations between the physico-chemical properties of the catalyst under working conditions and its performance. This knowledge is vital in a catalyst development program [1], bridging the identification of promising materials in the primary screening phase and the scale up of the catalytic process (Fig. 1). As concluded by NICE [2], progress in this direction is a primary need to strengthen the competitiveness of

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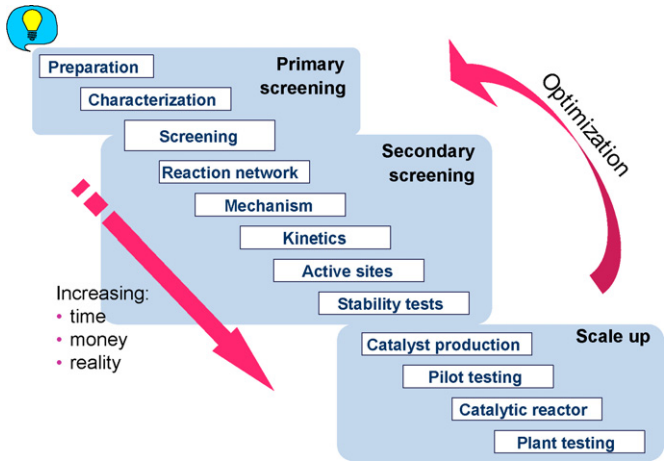

Fig. 1. Stages in a catalyst development program.

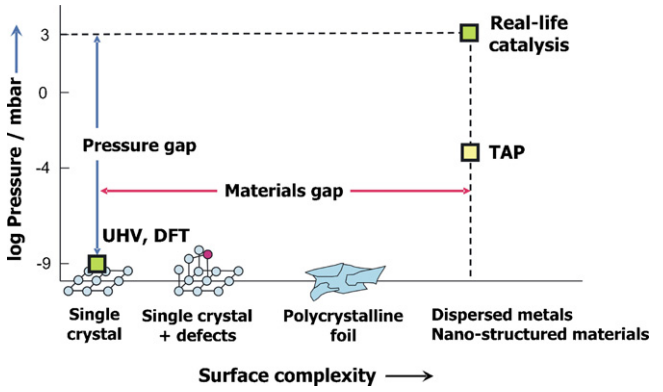

Fig. 2. Pressure–materials diagram indicating the position of the various approaches to investigate mechanisms and kinetics of heterogeneously catalyzed reactions.

the chemical industry. The Edisonian-based approach of high-throughput catalyst synthesis and testing dramatically accelerates the preparation and evaluation of new materials, and potentially the rate of catalyst discovery, but ultimately does not offer the required structure–activity relationships for rational catalyst design.

Traditional steady-state techniques operating at or near ambient pressure have been successfully applied for kinetic studies, but they are victim of their own simplicity and lack of molecular detail due to the low time resolution (in the order of seconds). Steady-state testing convolutes the reaction mechanism into a few complex steps that cannot be subdivided further using the experimental data. Consequently, they lead to macrokinetic models, which provide an integrated description of the reaction system by means of the analysis of the global behavior of the catalyst [3]. The latter models cannot be confidently applied to predict the reactor performance in a wide range of operating conditions. Substantially improved knowledge of the catalytic events can be obtained by adaptation of spectroscopic techniques in flow reactors, enabling to monitor the catalyst in action (coined as *operando* spectroscopy) [4].

In the preceding several years, significant advances have been made to acquire a deep molecular-level understanding of catalytic processes. The emphasis of surface science has been the development and application of methods to determine surface composition and structure [5,6]. A common approach is to fabricate a model catalyst with a well-defined surface, which is characterized with atomic precision, followed by exposure to reactants. Representative here is the application of (modulated) reactive molecular beam surface scattering, which enables to gain insights into the kinetics and dynamics of surface reactions under controlled conditions in ultra-high vacuum (UHV) at specific catalytic centers [7]. The high vacuum is necessary to form the molecular beam. Moreover, surfaces have to be regular enough so that the direction of rebound of the reactant gas molecules can be directed towards the aperture of the mass spectrometer. Complementarily, DFT-based quantum chemical techniques have experienced notable progress too, providing valuable information on the structure of the (potential) active centers and the energy of adsorbates interacting with them. In addition, detailed reaction paths can be derived, which are characterized by kinetic parameters of the elementary steps involved [3,8].

Fundamental knowledge generated using these advanced methodologies is often not effectively extrapolated to the particular industrial process. A sensible reason for this stems from the extremely opposite situation of both "real-life" and "UHV" approaches in the pressure–materials diagram in Fig. 2. The complexity of a commercial catalyst is enormously higher as compared to model surfaces, viz. single crystals applied in surface science as well as in computational methods (materials gap). In addition, surface science techniques operate under ultra-high vacuum (typically 10^{-8} to 10^{-9} mbar) as compared to pressure conditions in the real-world process (pressure gap). The idealization with respect to specimen structure and pressure regime might induce severe deviations, e.g. that certain reaction pathways observed in the industrial reactor are undetectable under UHV.

An example to illustrate the relevance of pressure and materials gaps in mechanistic investigations is the oxidation of ammonia over PGM (platinum group metals) catalysts in nitric acid production. This is one of the highest temperature (1023–1073 K) and shortest contact time (10^{-3} to 10^{-4} s) processes in the chemical industry, yielding NO with a high selectivity (95–97%) and N_2 and N_2O as by-products [9]. In spite of the high catalyst efficiency, this process is the largest source of N_2O in the chemical industry, and policies and regulations are being enforced to mitigate emissions of this harmful gas. Accordingly, a proper understanding of the origin(s) of N_2O becomes a need of practical relevance. The difficulties for assessing the mechanism of the high-temperature ammonia oxidation with traditional experimental methods at ambient pressure are principally caused by the extreme operating conditions, leading to complex phenomena at the reactor level (ignition, extinction, oscillations, hysteresis) [10,11] and the catalyst level (surface reconstruction) [12]. These aspects seriously complicate kinetic analyses. Controlled experiments have been conducted using molecular beams over Pt single crystals, providing valuable mechanistic information of the reaction in the temperature range of 300–1700 K [13–17]. The outcome of these

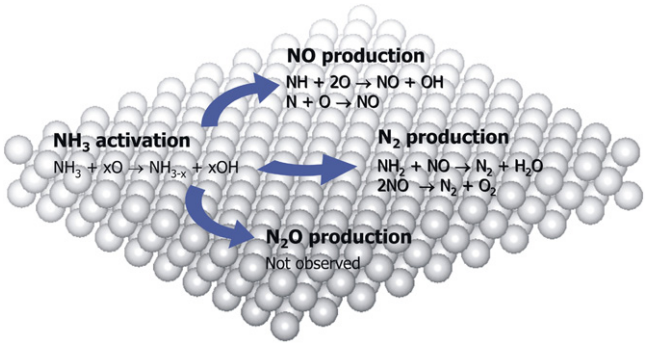

Fig. 3. Surface science studies with molecular beams have provided valuable insights into the mechanism of NH_3 oxidation to NO and N_2 over Pt single crystals, but N_2O was never detected and thus its formation was not discussed.

investigations, which is schematically represented in Fig. 3, shed light on reaction pathways towards NO and N_2. However, the robustness of this approach for achieving an accurate description of the overall mechanism can be questioned, since N_2O was never detected as a product in UHV studies.

An alternative strategy for mechanistic studies involves the application of transient methods. Dynamic testing allows the reaction to be analyzed as individual steps, giving more insight into the functioning of the catalyst. Transients are introduced into a system by perturbing one or more state variables, i.e. pressure, temperature, composition, and flow rate [18–20]. The temporal analysis of products (TAP) reactor belongs to this group of techniques. Several reviews have thoroughly described the principle and operation of the TAP reactor, the associated theoretical framework, and examples of application in heterogeneous catalysis [21–24]. The main attractiveness of the TAP technique is namely associated with the sub-millisecond time resolution, which makes it a powerful approach to study mechanisms, kinetics, and transport phenomena of heterogeneously catalyzed gas–solid reactions at near-to elementary level. In a broader perspective, we can illustrate the main benefits of the TAP technique attending to its position in the pressure–materials diagram in Fig. 2. The technique enables the investigation of model surfaces as well as practical catalysts. Besides, the peak pressure in the reactor can reach values in the order of 1 mbar, i.e. up to 9 orders of magnitude higher than pressures typically applied in UHV techniques. Both features bring the TAP reactor into a privileged situation among methods used for mechanistic and kinetic investigations, at the boundary between traditional steady-state flow techniques and surface science techniques with model surfaces in ultra-high vacuum. In direct reference to the above example, we shall demonstrate that TAP studies made it possible to elucidate pathways leading to N_2O in the high-temperature NH_3 oxidation over noble metal catalysts.

2. Brief history

The temporal analysis of products reactor was originally created to assist catalyst development and characterization at Monsanto. The idea was conceived by John T. Gleaves and his team in 1978–1979 and the first prototype was completed in 1980. In 1983 the system was redesigned and two new systems were built at the Monsanto Company in St. Louis. The technique was introduced to the scientific community during a presentation at the Chemical Conference of the Pacific Basin Chemical Societies in 1984 [25]. The first application disclosing the apparatus for carrying out and studying heterogeneously catalyzed chemical reactions was patented in 1986 [26], which later derived into additional patents claiming the method [27]. In 1987, Gleaves designed and built the prototype of the TAP-1 system. The latter was developed into a commercial instrument by Autoclave Engineers: 6 TAP-1 units were sold and then exited the business. After that Mithra Technologies was founded and in parallel the TAP-2 system was designed and patented by Gleaves [28–30]. The first TAP-2 reactor was built in 1992 and since then 14 units have been installed (4 in industrial laboratories). Besides the system commercialized by Mithra, various universities and research centers developed home-made TAP-like set-ups during the late 1990s. A noteworthy example is the Multitrack (Multiple Time Resolved Analysis of Catalytic Kinetics) system, developed in the group of Profs. J.A. Moulijn and F. Kapteijn at the Delft University of Technology [31].

3. Description and operation

The TAP experiments are performed in vacuum with very low amount (0.01–10 nmol) of reactants, strongly differing from conventional switch or pulse experiments. As schematically shown in Fig. 4, TAP reactors have four principal components: (i) high-speed pulse valves, (ii) the micro-reactor, (iii) the high-vacuum system, and (iv) the quadrupole mass spectrometer (QMS). Differently to the original TAP-1 reactor, the high-speed pulse valves and the micro-reactor in the TAP-2 reactor are not located in the vacuum chamber. Besides, the analytical probe in the TAP-2 is physically closer to the reactor outlet. The latter improvement is of vital importance for achieving high detection sensitivity and time resolution. Fig. 5 shows a photograph of the latest TAP-2 reactor installed at the ICIQ (Tarragona, Spain) in 2006.

The four high-speed pulse valves mounted in the manifold are electro-magnetically driven by activating a wire coil with a short current pulse. The current pulse produces an intense transient magnetic field that attracts a magnetic disk, which is attached to the valve stem. During the pulse the valve stem lifts out of the valve and allows a small quantity of gas to flow out. When the magnetic field collapses, a spring located behind the magnetic disk forces the stem tip back into the valve seat. Gas-phase molecules enter the micro-reactor, diffuse through it, and react on the catalyst. The components in the pulse leaving the micro-reactor are analyzed by mass spectrometry with high time resolution ($<10^{-3}$ s). The analysis can be done in time-resolved or mass-scan modes. Since the QMS requires at least 10 μs for switching between different atomic mass units (amus), only 1 amu per pulse can be monitored for achieving a high time resolution. In order to monitor all feed components and reaction products during a sequence of pulses, the QMS switches from the measured amu to the next one after the data

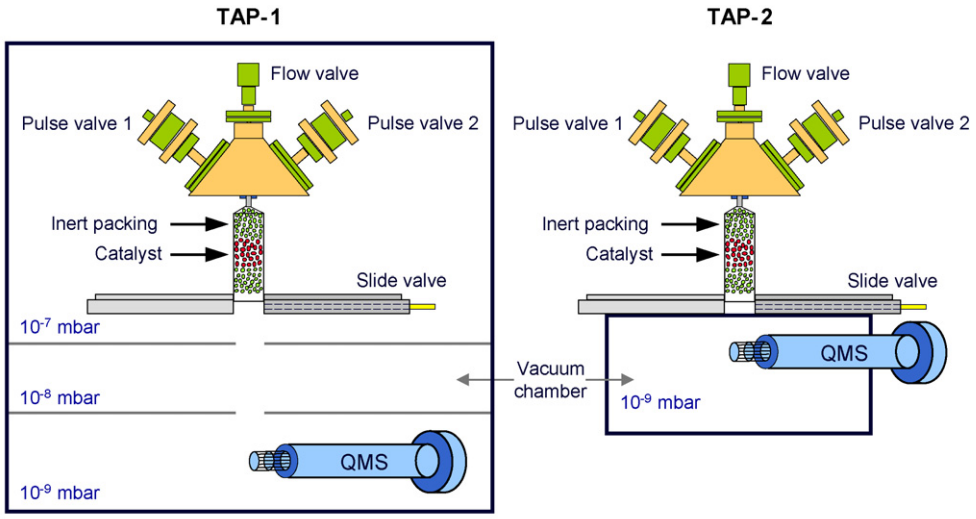

Fig. 4. Simplified scheme of the TAP-1 and TAP-2 reactor systems.

collection interval is completed. The limitation of monitoring a single amu per pulse can be overcome by installing numerous spectrometers. For example, the Multitrack system incorporates four QMS units in-line with reactor axis, although they are positioned at different distances so displaying different sensitivity [31]. DuPont developed a novel reactor design based on a linear time-on-flight mass spectrometer (TOF-MS) for measuring multiple masses with millisecond time resolution, but it did not provide the level of sensitivity desired.

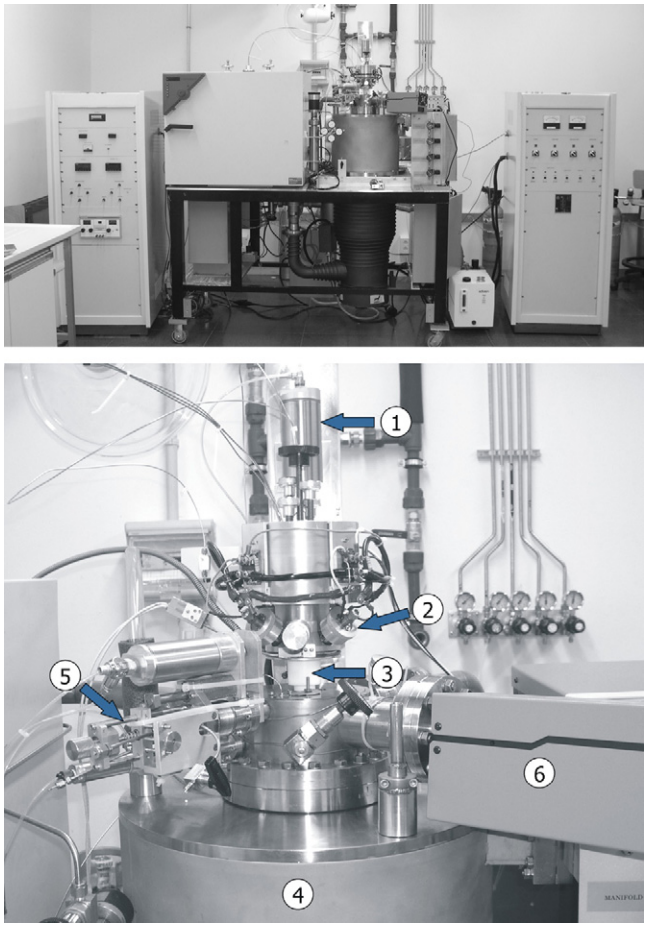

Fig. 5. General photograph of the TAP-2 system (top) and detail of the manifold (bottom): (1) continuous flow valve, (2) high-speed pulse valve, (3) micro-reactor, (4) vacuum chamber with liquid-nitrogen trap, (5) slide valve, and (6) quadrupole mass spectrometer.

Fig. 6 illustrates the types of transient experiments that are typically conducted in the TAP reactor. In *probe* experiments, several (ca. 100) low-sized (10^{13} to 10^{14}) pulses of a certain composition are introduced into the micro-reactor. Due to the small amount of reactant(s) dosed, the catalyst state is not significantly changed. These experiments are referred to as state-defining and provide intrinsic kinetic information (see, e.g. [32–36]). In *multipulse* experiments, a large number of 1000–10,000 pulses are introduced to the micro-reactor. These are referred to as state-altering, since the surface state of the catalyst is modified throughout the experiment. Multipulsing is suitable for deriving information on the catalyst ability to

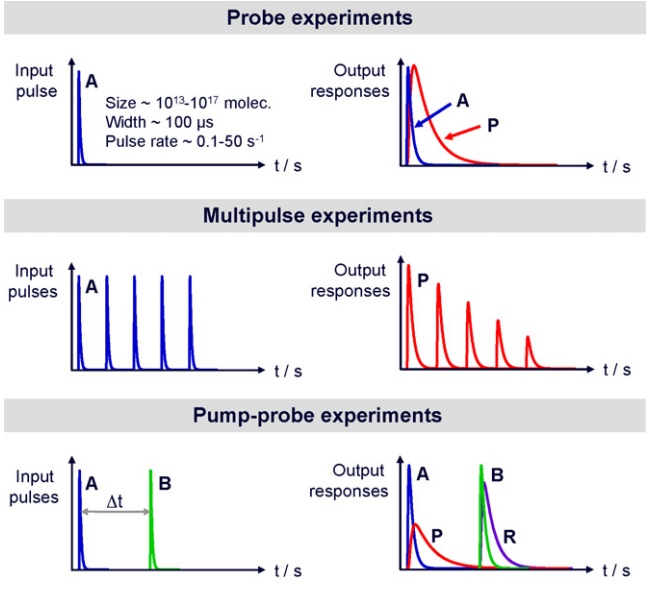

Fig. 6. Operating modes in the TAP reactor.

adsorb or dissociate the pulsed gases, e.g. making it possible to determine the concentration of active sites for O_2 activation over Na/CaO [37] and for N_2O decomposition over iron-containing zeolites [38]. Moreover, multipulse experiments are useful to probe the reactivity and selectivity of species for the catalytic reaction. For example, C_3H_8 multipulsing over vanadium-based catalysts made it possible to conclude that not only surface but also bulk lattice oxygen of VO_x species participate in C_3H_6 and CO_x formation via its migration from the bulk (Mars-van Krevelen mechanism) [39,40]. Similarly, the reactivity and amount of atomic oxygen species deposited by N_2O with CO can be ascertained [38]. In *pump-probe* experiments, two different reactants are sequentially pulsed from two pulse valves with different time delays (Δt) between the pulses. The time delay between the pulsed reactants can be varied from 0 to several seconds. In these experiments, information of the lifetime, reactivity and selectivity of adsorbed surface species can be obtained [38,41–43]. It should be pointed out that the manifold of the commercial TAP-2 reactor includes four pulse valves. This means that pump-probe experiments can be in principle performed using four different reactants, although to the best of our knowledge such a type of experiments have not been published in the literature.

4. Key advantages

The main advantages of the TAP technique for investigation of gas–solid processes associated with adsorption, reaction, and/or diffusion are summarized in Fig. 7. The technique has a sub-millisecond time resolution, which can be tuned by changing the reactor bed length and the width of the initial gas pulse. Due to this feature, the TAP reactor can be used for identification of reaction intermediates, determination of rate constants of elementary steps (single-event kinetics), elucidation of processes and their sequence in multi-step reaction networks, estimation of the number of active sites, manipulation and probing of catalyst surface oxidation states, etc. The nature of the specimen to be analyzed can be a single crystal or a practical catalyst, and full flexibility with respect to the physical shape of the catalyst (wire, foil, gauze, pellet, particle, monolith) is in principle possible. Operation in high vacuum enables to exclude the presence of external mass transfer limitations. Upon varying the pulse size, catalytic processes can be studied in different diffusion regimes. At pulse sizes $<10^{15}$ molecules, the gas transport through the catalyst bed is governed by Knudsen diffusion. In this case, the diffusivities of the individual components of a gas mixture are independent of pressure, concentration, or composition of the mixture. Besides, in this regime collisions between gas-phase molecules are minimized so pure gas–solid interactions are accounted for. Pulse sizes $>10^{15}$ molecules correspond to the molecular regime and potential gas-phase effects can be assessed. The peak pressure can be modulated with the pulse size, varying in the range of 0.01–1 mbar. This represents a great advantage with respect to UHV techniques, basically meaning that pressures 10^6 to 10^9 order of magnitude higher can be used in the TAP reactor. The use of small pulses, in the range of 0.1–10 nmol per pulse, makes it possible to ensure isothermal conditions, a critical aspect to study highly exothermic or endothermic reactions. This also minimizes the reconstruction of the catalyst surface. The application of small pulses is also highly advantageous when dealing with isotopes. The use of isotopic tracers is sometimes vital in the determination of reaction mechanisms, being the principle of SSITKA [19]. However, the latter technique operates under flow conditions, i.e. the usage of expensive isotopes is costly in comparison to the TAP reactor. Finally, the oxidation state of the catalyst surface can be manipulated and probed by application of multipulse or pump-probe experiments.

5. Achievements

Fig. 8 shows the evolution of the number of publications describing TAP experiments since the introduction of the TAP reactor by Gleaves et al. in 1988 [21]. The average number of publications yearly from 1995 is around 10. This technique has been applied for studying a wide range of heterogeneously catalyzed reactions, which are collected in Table 1. They include oxidative functionalization of light alkanes, ammoxidation of hydrocarbons, ammonia oxidation, NO_x reduction, reforming of alkanes, oxidation of volatile organic compounds, oxidative coupling of methane, CO oxidation, CO_2 reforming, catalytic cracking of hydrocarbons, and hydrogenation of unsaturated aldehydes. Moreover, diffusion in porous materials was also investigated by means of transient experiments in the TAP reactor. The variety of catalytic processes, materials

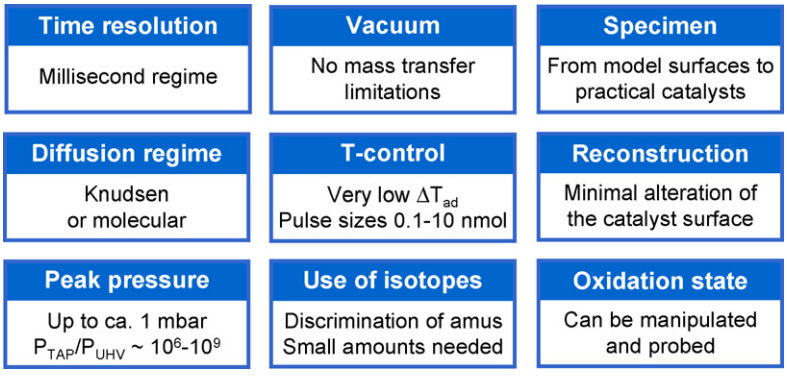

Fig. 7. Key advantages of the temporal analysis of products reactor.

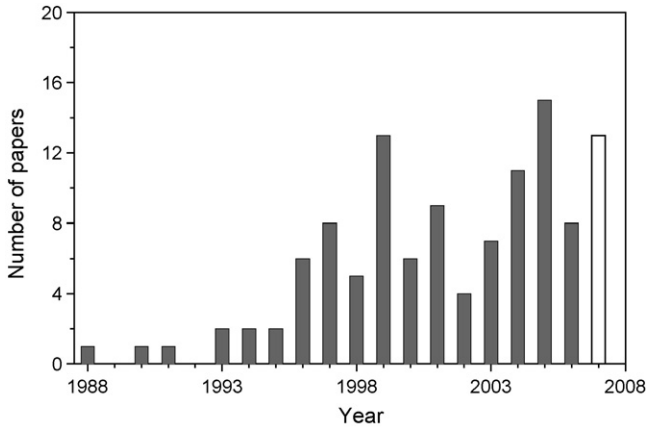

Fig. 8. Number of related papers in regular journals published in the period of 1988–2007 (*source*: SciFinder). The open box in 2007 only includes the papers in this Catalysis Today volume.

(metals, porous materials, bulk and supported mixed oxides) and geometries (particles, wires, foils, gauzes) makes the TAP technique a versatile tool for investigating gas–solid reactions.

Most of the published papers deal with the elucidation of reaction mechanisms. For example the application of isotopic labels and pump-probe (sequential) pulse experiments enabled to derive insights into the role of adsorbed and lattice species in the oxidative dehydrogenation of propane [39,42,44–47], oxidative coupling of methane [41,48,49], soot oxidation [50,51], methane conversion to syngas [52,53], ammoxidation of toluene [54], *n*-butane [55,56] and propane [57], ammonia oxidation [43,59–62], N_2O abatement [38,63] and N_2O-mediated selective oxidation of propane [46], and VOCs oxidation [58].

It is often reported that detailed reaction kinetics can be derived from transient experiments in the TAP reactor [32–35,45,66,83,90,94,97–100,102,105,107,126,127]. Kinetic evaluation of TAP experiments is typically based on analytical or numerical solution of partial differential equations describing chemical and transport processes in the micro-reactor. In their pioneering works, Gleaves et al. [21] introduced a simple analytical method for deriving activation energies of desorption as well as reaction constants of adsorption and desorption. These kinetic parameters are obtained from zero, first, and second moments of the experimental transient responses. Ten years latter, Gleaves et al. [22] have improved this method by taking into account catalyst location in the micro-reactor, temperature, and diffusion coefficients. A general theory of single pulse (state-defining) experiments has been developed by the Yablonsky, Gleaves, and coworkers [116,117,123,125]. The central part of this theory is so-called the global transfer matrix equation, which determines the dynamic behavior in the micro-reactor. The same group of researchers developed a new reactor model for TAP experiments, which is referred to as thin-zone reactor [114,122,124]. In this concept, concentration gradients across the catalyst bed can be neglected. Therefore, mass transport and chemical kinetics can be decoupled. Based on moment analysis, kinetic parameters of reversible adsorption as

Table 1
Summary of application fields of the TAP technique and catalytic materials studied

Topic	Catalysts	References
Adsorption and diffusion	Zeolites, γ-Al_2O_3, Rh/Al_2O_3, sulfated ZrO_2	[64–71]
Cracking/reforming of hydrocarbons	Zeolites, Pt-supported catalysts, MgO-Ru/C	[72–77]
Environmental catalysis		
Soot oxidation	La^{3+}-doped CeO_2, CeO_2	[50,51,78]
SCR of NO_x	Mordenite, Pt/ZSM-5, Ag/Al_2O_3	[79–81]
N_2O abatement	Pt, Pt–Rh, Fe-MFI	[35,38,63,82,83]
NO_x storage	Pt/BaO/Al_2O_3	[84]
VOC	U_3O_8	[58]
Hydrogenation		
Acroleine hydrogenation	Ag/SiO_2	[85]
Oxidation		
Ammonia oxidation	Pt, Pt–Rh	[43,59–62]
Oxidative coupling of methane	MgO, Na/CaO, Sm_2O_3	[34,41,48,49,86,87]
Propane ammoxidation		[57]
Propane conversion	$VCrMnWO_x$, Fe-ZSM-5, mixed vanadia-based oxides, VO_x/MgO, Sm_2O_3, VO_x/γ-Al_2O_3	[39,42,44–47]
Ethane conversion	Pt/Al_2O_3, Na/CaO, Sm_2O_3/CaO, Sm_2O_3	[88,89]
Propene oxidation	γ-Bismuthmolibdate, $Co_{10}Mo_{12}FeBiO_x$	[32,90,91]
Toluene ammoxidation	α-$(NH_4)_2[(VO)_3(P_2O_7)]_2$	[92]
Syngas production	Ru/Al_2O_3, MgO-promoted Ru/C, Pt/MgO, Rh black, Pt/ZrO_2, Pt/Al_2O_3, Pt	[52,53,93–97]
Toluene oxidation	VO_x/TiO_2, VO_x/SiO_2	[54,98,99]
o-Xylene oxidation	VO_x/TiO_2	[100]
Ethylene oxidation	Ag	[101,102]
n-Butane oxidation	$VOPO_4$, $(VO)_2P_2O_7$	[55,56,103–105]
n-Pentane oxidation	$(VO)_2P_2O_7$	[103]
CO oxidation	Au/Fe_2O_3, Au/$Ti(OH)_4$, Pt, $La_{1-x}Sr_xFe(Pd)O_3$	[31,106–108]
CH_4 oxidation	Ni/Al_2O_3	[33]
Theory and modelling		[21–24,91,102,109–125]

well as reversible and irreversible reactions can be obtained. The above analytical methods are fast but limited to simple first-order reactions. Numerical methods based on Laplace and fast Fourier transformations are also limited to first-order reactions. Alternatively, partial differential equations can be transformed into coupled ordinary differential equations by a spatial approximation and then integrated numerically. These methods are applicable for chemical reactions with different degree of complexity [110,128]. Kinetic parameters of complex reactions are obtained from non-linear regression analysis of the transient responses. Such approach is robust but time-consuming. A more detailed review on the kinetic evaluation of TAP experiments is given by Yves Schuurman in this volume of Catalysis Today.

6. Case study: N_2O formation in NH_3 oxidation

In 2002, Norsk Hydro (later Yara International) and the Institute for Applied Chemistry Berlin-Adlershof (later Leibuiz-Institut für Katalyse) initiated a research cooperation aiming at an improved mechanistic description of the high-temperature oxidation of ammonia over the industrially applied PGM gauzes. Our main target was the identification of reaction pathways leading to N_2O. As described in Section 1 of this manuscript, background studies using surface science techniques over single crystals were not able to identify N_2O as a reaction product, which is, however, extensively formed in the industrial ammonia oxidation process. One could suspect pressure and materials gaps to be the reason for this mismatch in product distribution. Understanding the origin of nitrous oxide is a fundamental prerequisite to subsequently design practical strategies in the ammonia burner for N_2O minimization. Based on previous experiences, we envisaged that the features of the TAP reactor could bridge the gap between UHV and real-life operation. Therefore, we systematically studied individual and combined interactions of NH_3, O_2, NO, and N_2O over PGM alloys in order to reconstruct the puzzle of processes taking place at the ammonia burner. Part of the outcome of these investigations has been published recently [43,59,60,62].

An important aspect for undertaking the study was the possibility to use the catalyst in its commercial form, i.e. as a gauze, thus excluding the materials gap due to the idealization of the surface. The excellent temperature control due to the very low heat production associated with typical pulse sizes should be stressed too. The adiabatic temperature rise upon oxidation of 10 nmol NH_3 (large pulse) to N_2 was estimated <3 K [43], making it possible to study this highly exothermic reaction under isothermal conditions. However, the ability to alter the peak pressure in the reactor (by changing the pulse size) and the use of isotopic tracers were the most crucial points for deriving mechanistic insights into the so-called loss reactions (N_2O and N_2 formation). Fig. 9 shows the transient responses of $^{15}N^{15}NO$ (46 amu) and CO_2 (44 amu) upon pulsing of a $^{15}NH_3$–O_2 mixture over a single piece of Pt–Rh gauze located in the isothermal zone of the TAP micro-reactor. The responses in the top figure were obtained in the Knudsen regime, i.e. using a pulse size of 10^{14} molecules (peak pressure 0.05 mbar). Nitrous

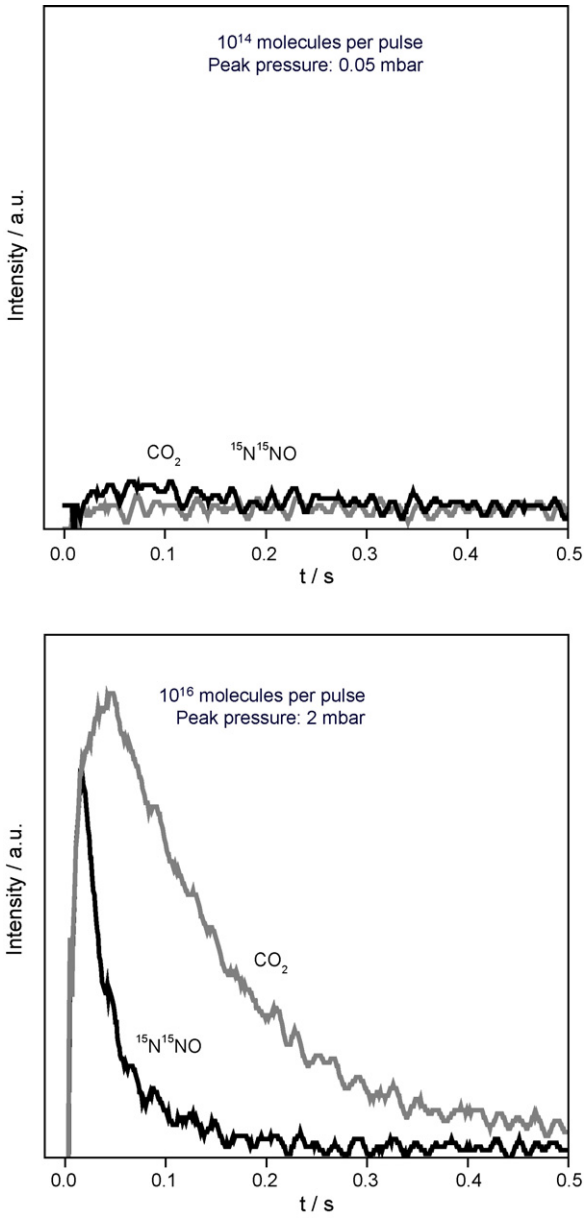

Fig. 9. Transient responses of $^{15}N^{15}NO$ (46 amu) and CO_2 (44 amu) upon pulsing of a $^{15}NH_3$:O_2:Ne = 1:2:1 mixture over Pt–Rh gauze at 1023 K using different pulse sizes (after Ref. [43]).

oxide was not detected at the reactor outlet. A pulses size of 10^{16} molecules, representative of the molecular diffusion regime (peak pressure 2 mbar) made it possible to visualize nitrous oxide for the first time (bottom figure). This result was exciting after a large number of unsuccessful attempts in the Knudsen regime. The latter is of course advantageous since only gas–solid interactions are accounted for. However, a non-catalytic contribution to the N_2O response in Fig. 9 was categorically excluded [59,60]. Therefore, we inferred that the pressure gap is the main cause for the invisibility of N_2O in previous molecular beam investigations (and in TAP studies with small pulse sizes).

The use of isotopically labeled $^{15}NH_3$ was also essential for appropriate results interpretation. As shown in Fig. 9, the CO_2

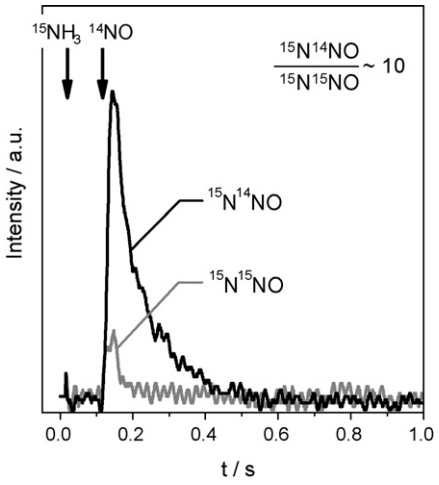

Fig. 10. Transient responses of $^{15}N^{15}NO$ and $^{15}N^{14}NO$ during pump-probe experiments with $^{15}NH_3$ and ^{14}NO over Pt–Rh gauze at 1023 K (after Ref. [60]).

transient response (resulting from oxidation of carbon deposits at the surface of the commercial gauze) is more prominent and very different in shape to that of $^{15}N^{15}NO$. Discrimination of both amus would not have been possible when using non-labeled $^{14}NH_3$, since the resulting $^{14}N^{14}NO$ and CO_2 have 44 amu. This can lead to faulty analysis of the results, since the gauzes were pretreated at 1273 K in pure O_2 flow for 2 h and as a result one would not expect carbon deposits to be still present on the catalyst.

Isotopic tracers were also essential to derive pathways leading to by-products formation (N_2O and N_2) [59,60]. To illustrate this, Fig. 10 shows the transient responses of two nitrous oxide isotopes ($^{15}N^{15}NO$ and $^{15}N^{14}NO$) upon sequential pulsing of $^{15}NH_3$ and ^{14}NO over Pt–Rh gauze at 1023 K (pulse size 10^{16} molecules). Production of N_2O is observed only in the pulse of nitric oxide and the relative amount of both isotopes revealed that the mixed $^{15}N^{14}NO$ was major as compared to $^{15}N^{15}NO$. The interpretation of this result was straight forward: nitrous oxide is not a primary product of ammonia oxidation, but stems from secondary interactions between NH_3 and NO. Upon interaction of O_2:NH_3 mixture over the catalyst, nitric oxide is readily formed and partially reduced by a coupling surface reaction between intermediate NH_x fragments and NO. The mechanism of N_2 production in the high-temperature NH_3 oxidation is also complex, since a number of reaction pathways are involved (NH_3 decomposition, NO reduction, NH_3–NO coupling) and, again, the use of isotopic tracers was essential for proper identification and discrimination [60]. The information coming out of this TAP project made it possible to accurately locate where loss reactions are mostly occurring in the gauze pack and the later has originated a fascinating research program to modulate catalyst composition and/or experimental conditions in the burners. It has been highly satisfactory for us to see how fundamental understanding derived from the TAP reactor has originated a renewed interest in ammonia oxidation, a process in industrial scale for over 80 years. We have used this success story to illustrate the powerful features of the temporal analysis of products, with particular focus on narrowing pressure and materials gaps. The TAP reactor can be generally embedded in industrial programs aiming at catalyst development and optimization, and this is supported attending to research centres in large companies commanding this transient pulse technique.

7. Conclusions and outlook

Since John T. Gleaves conceived the TAP reactor in the late seventies, this time-resolved transient pulse method has experienced important developments, becoming a powerful and versatile tool for investigating mechanisms of events associated with the heterogeneous catalytic process (diffusion, adsorption, reaction). The particular features of this time-resolved transient pulse method make it an advanced kinetic strategy at the boundary between traditional steady-state techniques and surface science techniques with model surfaces under ultra-high vacuum. Thus the often-highlighted pressure and materials gaps in mechanistic investigations can be narrowed, as exemplified by the case study of N_2O formation in NH_3 oxidation over noble metal catalysts. Accordingly, the TAP technique can be used in curiosity driven fundamental studies as well as in industrially oriented catalyst development programs.

A number of developments are going on to enhance the capabilities of the TAP reactor. For example, prompted by the high-throughput *fever*, the team of Mirodatos parallelized the TAP reactor by implementing a carrousel with 12 micro-reactors [127]. Integration of spectroscopic techniques in the TAP reactor to simultaneously monitor transient responses at the reactor outlet and the status of the catalyst surface is an *old* dream, not realized yet due to technical barriers regarding coupling time resolution of the methods and detection levels. In this respect, we should stress the exciting new development by Gleaves and coworkers in one of papers in this volume. These authors presently coupled the temporal analysis of products reactor system to an atomic beam deposition (ABD) system. In this manner, the surface of complex catalytic particles can be tailored at the atomic level, followed by kinetic characterization in the TAP-2 reactor. The goal of combining ABD with TAP experiments is to develop a method for establishing direct, reproducible correlations between changes in surface composition and changes in catalyst activity.

A related development is to adapt the micro-reactor of the TAP system for performing transient mechanistic studies over single crystals on a more regular basis. This opens new horizons in mechanistic understanding of heterogeneously catalyzed reactions, since the structure of the catalyst is well known and remains practically unchanged during TAP experiments. In this sense, a more fluid dialogue between the TAP and surface science communities could be beneficial in order to better understand mutual needs. A stronger interaction of TAP scientists and molecular modelling experts can be also fruitful.

Finally, an improved quantification of micro-kinetics based on TAP responses would make headway. Description of the performance of the steady-state processes from kinetic models

derived purely from TAP data is to be proven, and related studies are scarce. A first attempt to extrapolate the TAP-derived micro-kinetics to steady-state ambient pressure condition was recently made by us for the direct N_2O decomposition over iron-containing MFI zeolites [36]. With the present computing performance, such an approach can be applicable to more complex reactions.

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