Advanced techniques for characterization of heterogeneous catalysts

(4 credits/sp/op/Bologna)

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Transient analysis of catalytic reactions using isotopes.

Lecture outline

- Transient analysis of catalytic reactions using isotopes.
- Applications of Temporal analysis of products (TAP) in analysis of catalytic reaction mechanisms.
Transient analysis of catalytic reactions using isotopes

Steady-State Isotopic-Transient Kinetic Analysis (SSITKA) was principally developed by Happel [1], Bennett [2], and Biloen [3].

The technique utilizes isotopic-label substitution in the reactant and is able to maintain steady-state reaction under isotopic-transient conditions.

\[
\text{AB + CD} \rightarrow \text{AC + DB} \quad \text{vs.} \quad \text{A}^*\text{B + CD} \rightarrow \text{A}^*\text{C + DB}
\]

Therefore, unlike other transient techniques, SSITKA permits analysis of the steady-state kinetic behavior of the catalyst surface at temperature and pressure.

In **SSITKA (steady-state isotopic transient kinetic analysis)** it is common to consider the catalyst surface to be composed of a system of **interconnected pools**, also termed compartments, where each pool represents a homogeneous or well-mixed subsystem within the reaction pathway. A separate pool is assumed to exist for each unique adsorbed reaction-intermediate species or type of catalytically active site.

James G. Goodwin

It is assumed that there is essentially no mixing or holdup time associated with each pool or within the reaction pathway except for the residence time of a reaction-intermediate species adsorbed on the catalyst surface.

\[ N \] number of intermediate pools in series represents the steady-state reaction pathway


**Transient analysis of catalytic reactions using isotopes.**

\[ \overline{\lambda}_{i}^{R} \] is the steady-state abundance of the number of atoms of the isotope in each individual \( i \)-th pool \((i = 1, 2 \ldots n)\) where the overbar, \( \overline{\cdot} \), indicates a steady-state condition; 

\[ \overline{r}_{i}^{R} \] is the steady-state adsorption rates of reactant species \( R \) due to adsorption.

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Transient analysis of catalytic reactions using isotopes.

Introduction of a isotopic label

Now consider that an instantaneous and complete switch occurs at time, \( t = 0 \), in the isotopic labeling of species \( R \), \( R \rightarrow ^*R \), at the inlet of the reaction volume as indicated by \( ^*R \).  


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The new isotopic label in reactant species \( R \) progresses along the reaction pathway via reaction intermediates \( A \), resulting in a transient condition in the isotopic labelling for product species \( P \), \( P \rightarrow ^*P \).

Ultimately, all of the old isotopic label is displaced by the new isotopic label as indicated in figure below.

Final displacement of the old isotopic label by the new one

The distribution of the isotopic labels is dependent upon the steady-state transfer rates, between pools.
SSITKA is a powerful technique to determine \textit{in situ} kinetic information about the catalyst-surface reaction intermediates and mechanisms at steady state \textit{without substantial disturbance of the catalyst-surface behavior}, contrary to some other transient techniques.

Several examples of SSITKA applications

- CO oxidation over gold supported catalysts
- Oxidative coupling of methane
- NO reduction by ammonia
CO oxidation over gold supported catalysts. Transient analysis of catalytic reactions using isotopes

CO oxidation over nanogold supported on Al₂O₃ and TiO₂


Activity of gold nanoparticles to oxidize CO depends on their size

It has been found that differing kinetics of CO oxidation are observed when gold nanoparticles are supported on different metal oxides.

Main activities

- Isotopic transient analysis was used to determine a TOF based on the number of active intermediates on an operating catalyst.
- The ITA experiment involved making a step change in the isotopic content of one of the reactants (CO in this case) at steady-state reaction conditions.
- The pressure, temperature, total flow rate, and product composition were maintained during this change.
- The transient response of the isotopically labeled product (CO₂) was monitored by mass spectroscopy.
**CO oxidation over gold supported catalysts**  
*Transient analysis of catalytic reactions using isotopes*

**Schematic representations of the reactor system used**

For CO isotopic transient analysis  
For CO₂ transient analysis

**Global kinetics of CO oxidation**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{TOF}^b )</th>
<th>( \varepsilon )</th>
<th>( \alpha_{\text{O}_2} )</th>
<th>( \alpha_{\text{CO}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/TiO₂</td>
<td>0.34</td>
<td>29</td>
<td>0.25</td>
<td>0.20</td>
</tr>
<tr>
<td>Au/Al₂O₃</td>
<td>0.18</td>
<td>8</td>
<td>0.52</td>
<td>0.15</td>
</tr>
</tbody>
</table>

\( \text{TOF}^b \) is the global reaction rate per Au atom in the catalyst normalized by the fraction of metal exposed.

The fraction of Au exposed was estimated from the inverse of the surface-average Au particle size determined by STEM (3.4 nm for Au/TiO₂ and 3.8 nm for Au/Al₂O₃), corresponding to a dispersion of 29% for Au/TiO₂ and 26% for Au/Al₂O₃.

The slight dependence of the reaction rate on the reactant partial pressures suggests that the adsorption of O₂ and CO is not highly competitive as a result of separate adsorption sites and/or very low surface coverages.
Transient analysis of the effect of supports on main residence time of C-species leading to CO₂ formation

\[ ^{12}\text{CO} + \text{O}_2 + \text{Ar} \rightarrow ^{13}\text{CO} + \text{O}_2 + \text{He} \]

The average residence time of surface intermediates (\( \tau \)) leading from CO (the isotopically labeled reactant) to CO₂ is given by

\[ \tau = \int_{0}^{\infty} [F_2 - F_0] \, dt. \]

We can prevent readsorption of produced CO₂ by introduction of CO₂ into the reaction mixture!
Influence of flow rate and CO$_2$ content on residence time

The concentration of cofed product should be sufficient such that $\tau$ is independent of product concentration.

0.9 mol CO$_2$ is sufficient to block CO$_2$ readorption

To estimate the contribution of readorption and secondary reactions of CO$_2$ that may have been present during the isotopic transient analysis of CO oxidation.

CO$_2$ switching experiments were performed without the presence of CO.
The value of $\tau$ corrected for CO$_2$ readsorption ($\tau_{\text{corr}}$) is a good approximation of the intrinsic activity of the catalytic sites, as determined by:

$$\text{TOF}_{\text{intr}} = 1 / \Delta \tau$$

The intrinsic TOF ($\text{TOF}_{\text{intr}}$) provides an upper bound because it is based on the actual surface concentration of intermediates under reaction conditions. But some part of the active surface sites could be not saturated at the time of the isotopic switch.

However, the classical calculation of TOF involves the total number of surface metal atoms. Because not all of the surface atoms may participate in the reaction, the conventional TOF provides a lower bound on the normalized rate.

The moles of reactive surface intermediates per mole of Au, $N_{\text{CO}_x}$, was calculated using the following steady-state mass balance:

$$N_{\text{CO}_x} = \Delta \tau \times R_{\text{CO}_2}$$

where $R_{\text{CO}_2}$ is the steady-state rate of CO oxidation per mole of Au atoms.

The surface coverage of reactive intermediates, $\theta_{\text{CO}_x}$, can then be calculated from $N_{\text{CO}_x}$ using the Au dispersion

$$\theta_{\text{CO}_x} = \frac{N_{\text{CO}_x}}{\text{Au dispersion}}$$
Calculated kinetic parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T$ (K)</th>
<th>Global reaction rate ($\frac{\text{mol CO}_2 \text{ mol}^{-1} \text{ s}^{-1}}{\text{mol Au}^{-1}}$)</th>
<th>$t$ (s) w/reaction</th>
<th>$t$ (s) w/o reaction</th>
<th>$\Delta t_b$ (s)</th>
<th>TOF$_{\text{kin}}$ $^c$</th>
<th>$\theta^{\text{CO}_2} d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/TiO$_2$</td>
<td>303</td>
<td>0.44</td>
<td>0.62</td>
<td>0.37</td>
<td>0.25</td>
<td>4.1</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>0.32</td>
<td>0.67</td>
<td>0.35</td>
<td>0.32</td>
<td>3.1</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>273</td>
<td>0.10</td>
<td>0.87</td>
<td>0.60</td>
<td>0.27</td>
<td>2.7</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>261</td>
<td>0.06</td>
<td>0.94</td>
<td>0.59</td>
<td>0.35</td>
<td>2.8</td>
<td>0.07</td>
</tr>
<tr>
<td>Au/Al$_2$O$_3$</td>
<td>343</td>
<td>0.10</td>
<td>0.92</td>
<td>0.41</td>
<td>0.51</td>
<td>2.0</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.08</td>
<td>0.88</td>
<td>0.45</td>
<td>0.43</td>
<td>2.3</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>292</td>
<td>0.07</td>
<td>1.22</td>
<td>0.73</td>
<td>0.49</td>
<td>2.0</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>272</td>
<td>0.05</td>
<td>1.39</td>
<td>0.86</td>
<td>0.52</td>
<td>1.9</td>
<td>0.10</td>
</tr>
</tbody>
</table>

$^a$ Experimental conditions: 1.2 atm total pressure, He:CO:O$_2$:Ar = 95:3:2:0.7.

$^b$ Difference between $t$ with and without CO oxidation.

$^c$ Defined as $\Delta t^{-1}$.

$^d$ Fractional Au coverage of active intermediates based on 29 and 26% Au dispersions for Au/TiO$_2$ and Au/Al$_2$O$_3$, respectively.

Some conclusions (1)

- After correcting for CO$_2$ readsorption/secondary reactions, it was discovered that $t$ was independent of temperature for both samples.
  
  The surface reaction of adsorbed CO with surface oxygen was nearly unactivated.

- The coverage of carbon-containing intermediates leading to CO$_2$ was found to actually increase with temperature.
  
  - More carbon-containing intermediates are found on Au/TiO$_2$ compared with Au/Al$_2$O$_3$ at higher temperatures, which is related to the higher observed activation energy on Au/TiO$_2$.
  
  - $\theta^{\text{CO}_2}$ is suspected to be a function of the availability and subsequent activation of O$_2$.
CO oxidation over gold supported catalysts

Transient analysis of catalytic reactions using isotopes

Some conclusions (2)

- The higher global rate for Au/TiO₂ was the result of both a higher TOF$_{\text{int}}$ and a greater number of active intermediates.

- Two general roles of the metal oxide support have been proposed:
  - to influence the electronic properties of the Au nanoparticles and
  - to supply adsorption sites.

- The ability of Au/metal oxide to activate O₂ is a key feature in determining the global reaction rate.

Oxidative coupling of methane

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Advanced techniques for characterization of heterogeneous catalysts. Part 3

Oxidative coupling of methane

\[ 2\text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O} \]

It is an alternative way for ethane and ethene production

\[ \text{C}_2\text{H}_6 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \]

\[ \text{CxH}_y + \text{O}_2 \rightarrow \text{CO} + \text{CO}_2 + \text{H}_2\text{O} \]

Undesired reaction

So far, the maximum yield obtained is about 20%, which means that the process is economically unfeasible.

Therefore, in order to optimize the catalyst performance, insight into the heterogeneous and homogeneous steps contributing to the mechanism is required.

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Transient analysis of catalytic reactions using isotopes

**SET-UP**

Gases

\( \text{O}_2, \text{CH}_4, \text{and CO}_2 \) were used as feed gases.

\( ^{16}\text{O}_2, ^{13}\text{CO}_2, \) and \( ^{13}\text{CH}_4 \) were used in the isotope step experiments.

Once the steady state of the reaction has been reached, a step change from an unlabeled reactant to an isotopically labeled one is made without disturbing the surface reaction (i.e., pressure, temperature, and other reaction conditions are kept constant).

Catalysts

MgO, fresh and lined-out lithium-promoted MgO, and tin/lithium-promoted MgO
Oxygen isotopes responses after step $^{16}\text{O}_2 \rightarrow ^{18}\text{O}_2$ (no reaction) over lined-out Li/Sn/MgO

- In the absence of reaction, the $^{16}\text{O}_2$ response is slow compared to the inert Ar response. A strong interaction of oxygen with the catalyst.
- The formation of $^{16}\text{O}^{18}\text{O}$ indicates the dissociative adsorption of oxygen.
- Relatively stable level of $^{16}\text{O}^{18}\text{O}$ after reaching a maximum points to an additional oxygen source available for exchange besides oxygen in the gas phase.

Oxidative coupling of methane

Transient analysis of catalytic reactions using isotopes

Oxygen isotopes responses after step $^{16}\text{O}_2/\text{CH}_4 \rightarrow ^{18}\text{O}_2/\text{CH}_4$ (reaction) over lined-out Li/Sn/MgO

The $^{16}\text{O}_2$ response under reaction conditions initially displays a rapid relaxation, not significantly different from the inert response.

This could be the result of the presence of water, carbon dioxide, or a carbonate phase, diminishing the number of exchange sites for oxygen.
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Oxidative coupling of methane

Transient analysis of catalytic reactions using isotopes

$^{12}\text{CH}_4$, $^{12}\text{C}_2\text{H}_4$, and $^{12}\text{CO}_2$ responses after step change $\text{O}_2/^{12}\text{CH}_4 \to \text{O}_2/^{13}\text{CH}_4$

over lined-out Li/Sn/MgO

$\text{O}_2 + ^{12}\text{CH}_4 \to ^{12}\text{CH}_4 + ^{12}\text{CO}_2$

- $\text{C}_2\text{H}_4$ and $\text{CH}_4$ - slight interaction with catalyst
- $\text{CO}_2$ - strong interaction of carbon species producing $\text{CO}_2$

(T = 750 °C; feed ratio ($\text{CH}_4/\text{O}_2$) = 4)

![Graph showing $^{12}\text{CO}_2$ (model) and $^{12}\text{CH}_4$, $^{12}\text{C}_2\text{H}_4$, $^{12}\text{CO}_2$ fractions over time]

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Oxidative coupling of methane

Transient analysis of catalytic reactions using isotopes

Reaction mechanism used for describing the isotope step experiments over lined-out Li/Sn/MgO for the oxidative methane coupling

<table>
<thead>
<tr>
<th>Reaction step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $\text{O}_2 + 2^* \to ^{16}\text{O}^2$</td>
<td>Dissociative adsorption of oxygen</td>
</tr>
<tr>
<td>(2) $\text{CH}_4 + ^{16}\text{O}^* \to ^{16}\text{CH}_3^* + \text{OH}^*$</td>
<td>Formation of methyl radical on catalyst</td>
</tr>
<tr>
<td>(3) $\text{OH}^* + \text{OH}^* \to \text{H}_2\text{O} + 2^*$</td>
<td>Regeneration of adsorbed oxygen</td>
</tr>
<tr>
<td>(4) $\text{CH}_3^* + \text{CH}_2 \to ^{12}\text{C}_2\text{H}_6$</td>
<td>Formation of ethane in gas phase</td>
</tr>
<tr>
<td>(5) $\text{C}_2\text{H}_4 + ^{16}\text{O}^* \to ^{12}\text{C}_2\text{H}_2^* + \text{OH}^*$</td>
<td>Dehydrogenation of ethene to ethene by oxygen on the catalyst</td>
</tr>
<tr>
<td>(6) $^{12}\text{CH}_2^* + 2^* \to ^{12}\text{C}_2\text{H}_4 + \text{OH}^*$</td>
<td></td>
</tr>
<tr>
<td>(7) $\text{CH}_3^* + ^{16}\text{O}^* \to ^{12}\text{CH}_2\text{O}$</td>
<td>Formation of methoxy species on catalyst</td>
</tr>
<tr>
<td>(8) $\text{CH}_3\text{O}^* + ^{16}\text{O}^* \to ^{12}\text{CH}_2\text{O}^* + \text{OH}^*$</td>
<td>Transformation of methoxy species to carbon dioxide</td>
</tr>
<tr>
<td>(9) $\text{CH}_2\text{O}^* + 3^* \to \text{CO}_2 + 3\text{OH}^*$</td>
<td></td>
</tr>
<tr>
<td>(10) $^\circ \text{O} \to \text{O}_{\text{bulk}}$</td>
<td>Exchange between oxygen on catalyst surface and lattice oxygen in the bulk of the catalyst</td>
</tr>
</tbody>
</table>

Only reactions 1, 2, 4, 5, 7 and 10 are kinetically significant, while the other reactions are potentially instantaneous under the investigated conditions.

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Kinetic parameters for the kinetically significant elementary steps taken into account in the model above

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$3.5 \times 10^{-2}$</td>
</tr>
<tr>
<td>$k_2$</td>
<td>$1.3 \times 10^{-2}$</td>
</tr>
<tr>
<td>$k_3$</td>
<td>$1.75 \times 10^{-3}$</td>
</tr>
<tr>
<td>$k_4$</td>
<td>$5.1$</td>
</tr>
<tr>
<td>$k_5$</td>
<td>$2.73 \times 10^{-3}$</td>
</tr>
<tr>
<td>$k_6$</td>
<td>$5 \times 10^{-29}$</td>
</tr>
</tbody>
</table>

The kinetic parameter values obtained by simultaneous regression of the oxygen and methane isotope step experiments in the presence of reaction.

Some conclusions

Both in the absence and presence of reaction, oxygen interacts strongly with the catalyst.

Oxygen displays reversible dissociative adsorption and exchange between oxygen on the catalyst and lattice oxygen in the bulk of the catalyst.

The experiments under reaction conditions can be described satisfactorily only with a methoxy species ($\text{CH}_3\text{O}$) on the catalyst as intermediate in the reaction route to carbon dioxide.
Over the last 15 years it has been found that it is possible, over certain catalysts, to selectively reduce the NOx (without reducing O₂) in an O₂ rich feed using low levels of un-burnt hidrocarbons present in the vehicle exhaust.

Supported Pt catalysts have been found to be effective for this reaction at relatively low temperatures although the selectivity of the reaction to N₂O (rather than to N₂) is still a problem.

Transient experiments have been focused on the reaction mechanisms of NO reduction over different Pt including catalysts when different reductants are used.
Typical set-up for SSITKA experiments

In order to avoid any pressure jump under reactant switching and to keep reaction conditions constant!

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Transient analysis of catalytic reactions using isotopes

**NO+O₂+C₃H₈ reaction over Pt/SiO₂ at 220°C**

- Adsorption of propane on the surface is irreversible.
- Catalyst becomes more oxidized after propane removal – production of NO₂.
- CO₂ profile confirms that the Pt surface is covered with carbonaceous species under reaction conditions. The oxidation of these species is limited by the surface oxygen concentration.

**NO+O₂ reaction over Pt/SiO₂ at 70°C**

The treatment in H₂ increases content of species resulting in N₂ and decreases content of species resulting in N₂O. Surface species that lead to N₂O are unstable relative to those leading to N₂.
NO + O₂ reaction over Pt/SiO₂ at 70°C

NO + H₂ + Ar → Ar + H₂ (60s) → ^15NO + H₂

- The catalyst is more active for deNOx reaction being prereduced.
- The first N₂ molecules formed are DOUBLY LABELLED.
- The production of the mixed labelled fraction gradually becomes significant and then decreases.

NO + O₂ + C₃H₈ reaction over Pt/SiO₂ at 225°C. SSITKA

14NO + O₂ + C₃H₈ → 15NO + O₂ + C₃H₈

- 14N₂ and 14N₂O decrease directly following the switch.
- Mixed N₂O and N₂ pass through maxima before slowly decreasing to zero
- Doubly labelled products are observed.
Transient analysis of catalytic reactions using isotopes

NO+O₂+C₃H₈ reaction over Pt/SiO₂ at 225°C. SSITKA

Using data obtained, the $\alpha$ profiles (where $\alpha$ represents the fraction of heavy atoms in the gas phase of a particular molecule) can be calculated using the formula:

$$\alpha(N_2) = \frac{[^{15}N_2] + 0.5[^{15}N^{14}N]}{[^{15}N_2] + [^{15}N^{15}N] + [^{14}N_2]}$$

Isotopic exchange in N-species leading to $N_2O$ proceeds more fast. These species are less stable.

The coverage of the Pt surface with $N_2$ and $N_2O$ precursors can also be calculated from these plots. It is found that Pt is never more than 15% covered with intermediates which form $N_2$ or $N_2O$.

Further analysis of the profiles is hampered because they are very rapid.

Transient analysis of catalytic reactions using isotopes

NO+O₂+H₂ reaction over Pt/SiO₂ at 70°C. SSITKA

Transient responses are far longer particular that for $N_2$!

There is difference between the $\alpha$(NO) profile and the Ar. This indicates that there is desorption of NO from the catalyst during reaction.

$\alpha N_2O=\alpha NO$ ! $N_2O$ containing a $^{14}N$ labelled atom can only be formed while gas phase $^{14}NO$ is present within the catalyst bed.
The individual concentrations of the various isotopic N\textsubscript{2} species can be studied directly after the isotopic switch (Initial Distribution of the Isotopic Molecules of Products – IDIMP), and as a function of time following the switch (Temporal Redistribution of the Isotopic Molecules of Products – TRIMP).

Every collection of molecules of the type A\textsubscript{2} (where there are TWO possible isotopes for each atom (A or A\textsuperscript{*})) forms a mixture of molecules containing:
- 0 heavy atoms (AA);
- 1 heavy atom (AA\textsuperscript{*});
- 2 heavy atoms (A\textsuperscript{*}A\textsuperscript{*}).

The abundance of each type of these species will depend on:
- the overall concentration of the heavy atom in the mixture (like \(\alpha\)),
- as well as on the extent of isotopic equilibration within these molecules.

The normalized equilibrium concentration of an isotopic molecule Ai\*A2-i can be calculated from equitation:

\[
\lambda_{i}^{eq} := \binom{2}{i} \alpha^{i} (1 - \alpha)^{2-i}
\]

Where \(\lambda_{i}^{eq}\) represents normalized equilibrium concentration of the N\textsubscript{2} molecules containing i-heavy atoms.
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**Transient analysis of catalytic reactions using isotopes**

**Analysis of Distribution of Isotopic Molecules of Products**

The TRIMP plots represent the deviation on the normalized $^{14}\text{N}^{15}\text{N}$ and $^{15}\text{N}_{2}$ concentrations from their ISOTOPIC EQUILIBRIUM normalized at each value of $\omega(N_{2})$. Below the difference between the expected and the observed isotopic molecules of $N_{2}$ is shown.

The most abundant $N_{2}$ species at this time is the mixed labelled $^{14}\text{N}^{15}\text{N}$ species (around 85%).

So, there are TWO routes to the production of $N_{2}$.

- Weakly bonded NO interacts with a reduced species on the surface. This process leads to the over production of $^{14}\text{N}^{15}\text{N}$ species (relative to its isotopic equilibrium level).

  \[
  ^{15}\text{NO} + ^{14}\text{N}-\text{X} \rightarrow ^{15}\text{N}^{14}\text{N} + \text{O-}\text{X}
  \]

- Two identical species on the surface interact, both of each give one N atom to the $N_{2}$ molecule.

  \[
  ^{14}\text{N}-\text{Y} + ^{14}\text{N}-\text{Y} \rightarrow ^{14}\text{N}_{2} + \text{Y+Y}
  \]

The sequence of these steps leads to the underproduction of the $^{14}\text{N}^{15}\text{N}$ species later on in the switch and is responsible for the appearance of the unlabelled $^{14}\text{N}_{2}$ species in the IDIMP.
Applications of Temporal analysis of products (TAP) in analysis of catalytic reaction mechanisms

The temporal analysis of products (TAP) reactor system is an important new tool for investigating “gas–solid” reactions, particularly reactions on industrial catalysts.

Originally created by John T. Gleaves in 1988 (in Monsanta) and later modified by him in 1997, the TAP technique found an application in many areas of chemical kinetics and chemical engineering, especially due to its submillisecond time resolution.

The key feature which distinguishes it from other pulse experiments is that no carrier gas is used and gas transport is the result of a pressure gradient.
Later, a new improved apparatus, called TAP-2 reactor system, has been developed, aimed at extracting kinetic information from a heterogeneous catalytic system and revealing mechanisms of complex heterogeneous catalytic reactions.

This is accomplished by injecting an extremely narrow gas pulse into one end of a microreactor and continuously evacuating the other end. 10^{13} to 10^{17} molecules/pulse, with a pulse width of 250 µs, and a pulse frequency between 0.1 and 50 pulses/s.

The TAP-2 reactor system can be used to perform transient as well as steady-state experiments at pressures ranging from 10^{-7} to 250 kPa, and temperatures ranging from -70°C to 930°C.

Pulse content 10^{13} to 10^{17} molecules/pulse,
pulse width of 250 µs,
pulse frequency between 0.1 and 50 pulses/s.

Such time resolution characteristics are unique among other kinetic methods.

Possible experiments include:

- high-speed pulsing;
- both single pulse and multipulse response;
- steady state isotopic transient kinetic analysis (SSITKA);
- TPD;
- and TPR.
Temporal analysis of products (TAP)

Schematic diagram of the TAP reactor

1 - High-speed beam valve,
2 - continuous flow valve,
3 - zero-volume manifold,
4 - catalytic microreactor, (all of these being situated in the reactor chamber),
5 - differential chamber,
6 - detector chamber.

In the TAP-2 system, the two devices are physically much closer, and as a result the detection efficiency of the TAP-2 system is much higher.

The movement of a gas pulse from the microreactor to the quadrupole mass spectrometer.

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In a typical pulsed mode experiment, the pulse mixture contains reactants and an inert gas as internal standard. Consequently,
- responses,
- exit flow time dependencies, for reactants, products, and inert are monitored.

For a typical experimental set-up only one gaseous component can be measured during one pulse. When more than one substance is of interest, the single-pulse TAP experiments must be repeated.

To provide simultaneous multisubstance measurements, gas leaving the reactor has to be analyzed using several mass spectrometers in line.
The TAP microreactor configuration which is the most commonly used, is the so-called "three-zone" configuration.

The catalyst zone is sandwiched between two beds of inert particles, called inert zones.

**The main advantage** of the three-zone TAP reactor is that the catalyst zone can be more easily maintained under isothermal conditions.

**Disadvantage.** It is difficult to maintain a uniform profile of the surface catalyst composition because of the gas concentration gradient, which is the driving force of diffusional transport. In multipulse experiments, the nonuniformity of the catalyst composition becomes significant.
**Temporal analysis of products (TAP)**

The “thin-zone” configuration of TAP reactor

The change of gaseous concentration across the thin catalyst zone can be neglected, and the catalyst composition can be considered as uniform.

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**Basic principles of TAP**

The basic principles of TAP follow:

- Well-defined Knudsen diffusion as a “measuring stick” for chemical reaction characterization.
- Insignificant change of the solid material during a single pulse experiment.
- Uniformity of the surface composition of the material across the active zone.
Temporal analysis of products (TAP)

**Knudsen diffusion as a “measuring stick”**

A common approach for extracting kinetic information is to measure the rate of chemical reaction using the rate of mass transport as a “measuring stick.”

Transport, however, is a complex process that involves both diffusion and convection and can be different in different parts of a catalytic system.

In traditional steady-state experiments, convectional transport that is supposed to be well defined provides a measuring stick and diffusional transport neglected.

In contrast, in a typical TAP experiment, the diffusion, particularly Knudsen diffusion, is the only transport mechanism, which obviously must not be eliminated.

In the Knudsen diffusion regime, the diffusivity is determined by

$$D_t = \frac{\varepsilon_b}{\tau} \frac{d_i}{3} \sqrt{\frac{8RT}{\pi M}}, \quad d_i = \frac{4\varepsilon_b}{3(1 - \varepsilon_b)} r_p.$$  

Thus, in the Knudsen regime, the transport of individual species is independent on the gas composition and the [G.S. Yablonsky et al. / Journal of Catalysis 216 (2003) 120–134 123] mass transport is well defined.

The exit flow is described by the standard diffusion curve when only diffusion occurs. In the “reaction–diffusion” case, the exit flow is changed, and this change is attributed to the reaction.
Temporal analysis of products (TAP)

**Insignificant change of the solid material during the pulse experiment**

A typical Knudsen pulse contains $10^{13}$ molecules or $10^{-10}$ moles. (be equivalent to $10^{-6}$ of the total surface area of 0.1 g sample with surface area 10 m$^2$/g)

So, the number of reactant molecules in a pulse is significantly smaller than the number of active sites of the catalyst, the catalytic system remains in the same state after the measurement.

Temporal analysis of products (TAP)

**Uniformity of the surface composition across the active zone**

This principle has to be considered as absolutely necessary in TAP studies because kinetic information corresponding to a given catalyst composition cannot be obtained directly when nonuniform catalyst states are probed.
The place of the TAP experimental method among other kinetic methods

Kinetic studies focus on the selection of an adequate rate expression and determination of the unknown rate parameters it contains. While steady-state experiments give a global picture of the reaction kinetics, transient experiments give information relative to the individual steps involved.

<table>
<thead>
<tr>
<th>Approaches</th>
<th>Uniformity of catalyst composition</th>
<th>Domain of conditions</th>
<th>Reliability of the information</th>
<th>Control of gaseous substance amounts stored/released by catalyst</th>
<th>Model-free or not</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSTR</td>
<td>Typically, it is assumed for the steady-state case</td>
<td>Normal conditions, industrial domain</td>
<td>Steady-state information is reliable; nonsteady-state information is not</td>
<td>No</td>
<td>Steady-state CSTR is model-free. CSTR + SSITKA is model-free. Nonsteady-state CSTR gives rise to errors.</td>
</tr>
<tr>
<td>PFR</td>
<td>No uniformity</td>
<td>Idem as CSTR</td>
<td>Both steady-state and nonsteady-state information are reliable</td>
<td>No</td>
<td>Steady-state PFR is model-free. Nonsteady-state PFR is not model-free.</td>
</tr>
<tr>
<td>TAP reactor</td>
<td>No uniformity (three-zone configuration)</td>
<td>The top of the “surface science” domain</td>
<td>Nonsteady-state information is reliable</td>
<td>Yes, especially for the thin-zone TAP reactor</td>
<td>The first modifications of TAP reactor are not model-free. The thin-zone TAP reactor gives model-free information using Y-procedure.</td>
</tr>
</tbody>
</table>

Advanced techniques for characterization of heterogeneous catalysts. Part 3

Some remarks

**Uniformity of the active zone**

In a CSTR, the disturbing effect of diffusion on the observed characteristics is minimized; diffusion is not eliminated but complemented by stirring.

In TAP experiments, convection is easily and completely eliminated, and diffusion is well defined.

**Domain of conditions**

CSTR and PFR reactors provide data obtained under temperature and pressure conditions which are close to the industrial conditions.

While the most appropriate TAP regime (Knudsen regime), in which the transport is well defined, is located within $10^{-2}$–$10^{-1}$ Pa.
**Temporal analysis of products (TAP)**

**Some remarks**

**Possibility to obtain relevant kinetic information**

CSTR and PFR are mostly used to obtain steady-state kinetic information. Nonsteady-state CSTR can be simulated via ordinary differential equations and even analytical solutions can be obtained sometimes. For the nonsteady-state regime in the PFR, it can be simulated using integrating partial differential equations.

In many cases, CST reactors have a “dead volume” inside or outside which influences the transient behavior!

The differential PFR can provide rich information using the step response experiments. However, the PFR time resolution is limited by the imposed step function of the reactant concentration in the carrier gas (several seconds).

In TAP experiments relaxation times as short as $10^{-4}$–$10^{-3}$ s.

**Advanced techniques for characterization of heterogeneous catalysts. Part 3**

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**Some remarks**

**Correspondence between observed kinetic characteristics and catalyst properties**

As result, using CSTR or PFR data, for both steady-state and nonsteady-state cases, it is difficult to directly relate the observed kinetic characteristics to the material properties even with application of SSITKA technique. When SSITKA data can be used to determine the amount of surface substances as well as the rates of their formation characterizing the given steady-state of the catalyst.

From other side In TAP experiments under Knudsen diffusion conditions many kinetic characteristics of complex catalytic materials can be obtained as a function of surface concentrations that do not change (or do not change significantly) during the kinetic characterization.
Some remarks

**Model-free data interpretation**

**CSTR**
The consumption rate of a reactant, $R$,

$$R(c) = \frac{F_v(c^0 - c)}{V_{cat}}.$$  
steady-state

$$R(c) = \frac{V_g}{V_{cat}} \frac{dc}{dt} - \frac{F_v(c^0 - c)}{V_{cat}}.$$  
nonsteady-state

**PFR**
An application of the differential method to nonsteady state PFR data is extremely difficult because of experimental errors.

**TAP**

\[ 1 - X = \frac{1}{\cosh(\psi) + \alpha \psi \sin(\psi)}, \quad \psi = \sqrt{\frac{l_3}{l_{cat}} \frac{D_{g,cat}}{k_{app}}}, \quad \alpha = \frac{D_{g,cat}}{D_{g,in}} \frac{l_3}{l_{cat}}. \]

\[ \text{Reaction-diffusion parameter} \]
\[ \text{Diffusional-geometrical parameter} \]

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Recently, a special procedure, the so-called **Y-procedure**, was developed by Yablonsky et al. for the analysis of data from the thin-zone TAP experiment.

The procedure allows us to determine the gas concentration and reaction rate in the active zone of TZTR.

The mathematical foundation of the **Y-procedure** is the Laplace-domain analysis. Transposition to the Fourier domain combined with time discretization and filtering of the high-frequency noise leads to an efficient practical method for the reconstruction of gas concentration in a nonsteadystate regime without any presuppositions about the kinetic dependence; i.e., it is a model-free procedure.
What is next?

There are two known kinetic strategies:

- **traditional experiment over industrial multicomponent catalysts under normal conditions** (CSTR and PFR, working in a steady-state or none steady-state regime);

- **surface science experiments** under high vacuum conditions mostly over single crystals with well-defined surfaces which are very different from the industrial multicomponent catalyst.

However, traditional applied kinetics and surface science kinetics are separated by a “pressure” and “material” gap.
The TAP approach can be defined as a “third kinetic strategy,” which focuses on the bridging of these “gaps” in the near future.

The TAP pulse-response pressure domain (10^{-2}–10^{-1} Pa) is located at the boundary between the traditional applied kinetics and surface science kinetics, and this domain can be extended.

TAP experiments are designed to measure kinetics under dynamic conditions and to obtain a spectrum of parameters corresponding to changes that occur in a catalyst.

TAP pulse response experiments can be performed on practical catalytic materials at pressures higher than those used in surface science experiments.

A state-altering experiment realized as a multi-pulse TAP experiment will provide both integral (total amounts of consumed/released substances) and differential (kinetic parameters) characteristics at any given catalyst state.