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CHARACTERIZATION AND REACTIVITY OF WORKING CATALYSTS

The combination of SSITKA and DRIFT spectroscopy techniques allows to evaluate parameters without perturbing the overall steady state of the **stabilized catalyst** and for example visualizing directly the accumulated species on the reacting surface.

This paper recalls the basics and experimental of these techniques and illustrates their implementation through case studies, related to challenging domains in heterogeneous catalysis.

When an heterogeneous catalytic system works under steady-state conditions (stable overall rate of the reaction), each reactive adspecies may be characterized by a mean lifetime on the solid. It may be postulated that this lifetime depends directly on the nature of the catalytic site; its reverse function gives straightforwardly the true reactivity (or effective turnover number) of the active site. Over the last decades, much use has been made of non-steady-

state kinetics to determine this true reactivity of working sites, unique information without which no reliable mechanism may be postulated. By changing rapidly experimental variables such as gas concentration or reaction temperature, one generates a perturbation of the system which tends to relax into a new steady state; from this dynamic response, the time constants of the surface processes and therefore the concentrations of the intermediate species become now directly measurable. These non steady-state kinetics may be

generated either in a single cycle (a single transient input signal) or in a periodical cycle mode (with repeated transient signals).

The bases of these transient techniques applied to heterogeneous catalysis were settled by Tamaru [1] and further reviewed by Bennett [2], Schwarz and Falconer [3]. In numerous cases, pools of inactive adspecies accumulated on the surface under steady-state conditions might start to participate to the reaction under non steady-state conditions due to deep changes in surface reactivity (e.g., restructuring). The extrapolation of kinetic data obtained in non-steady-state conditions to steady-state regime then requires delicate analysis.

A specific way to use non-steady-state kinetics has originally been developed by Happel [4], Biloen [5] and Mirodatos [6], referred to as Steady State Isotopic Transient Kinetic Analysis (SSITKA). It is based on the simple idea which consists of applying an isotopic transient signal like a step function at a catalytic reactor inlet in order to collect the elementary kinetic parameters of the reaction without perturbing the overall steady state of the stabilized catalyst. SSITKA was successfully applied to catalysis on metal (e.g. CO hydrogenation [5-9], benzene hydrogenation [10, 11] and ammonia synthesis [12]). Then it has been extended to oxidation catalysis (e.g., CH₄ oxidative dimerisation [13, 14] and partial oxidation to syngas [15], acrolein oxidation [16]), lean de-NO_x [17] and hydrogen purification [18]. Several recent reviews [19-22] demonstrate how this powerful technique can be applied to any kind of catalytic systems, providing the catalyst remains in a stable solid state. Combining this approach with in-situ characterization techniques like Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy adds major benefits such as visualizing directly the accumulated species on the reacting surface, in general more “spectators” than short lifetime “active intermediate” species.

This paper recalls the basics and experimental of these techniques and illustrates their implementation through case studies, related to challenging domains in heterogeneous catalysis.

Basics and experimental [4-6]

When applying an abrupt perturbation at the inlet of a catalytic reactor, the outlet relaxation to steady-state is a combination of i) the time of transfer through the reactor (hydrodynamics, inter-particles diffusion) and ii) the residence time on the catalyst (reactants adsorption/desorption, chemical transformation, products adsorption/desorption).

Let us consider a pseudo first order reaction:



with A as an active intermediate.

At steady-state: $r_P = k A_{SS}$ and $(dA/dt) = r_R - r_P = 0$, with r_R and r_P are the rate of reactant consumption and product formation, respectively. A_{SS} is the steady-state concentration of A. For generating unsteady-state, R is stopped at reactor inlet ($r_R = 0$):

$dA/dt = -r_P = -kA(t)$, a differential equation which can be integrated as:

$$A(t) = A_{SS} \exp(-kt)$$

$$r_P(t) = r_{PSS} \exp(-kt)$$

$$A_{SS} = 1/k r_P = \tau r_P \text{ or } k = 1/\tau$$

with τ being the mean residence time of A on the catalytic surface. However, in most cases, pools of active intermediates are not stable under transient conditions (spectator adspecies may become active or vice versa). By replacing reactant R by its labeled equivalent *R , the overall steady-state is maintained but the transient change in

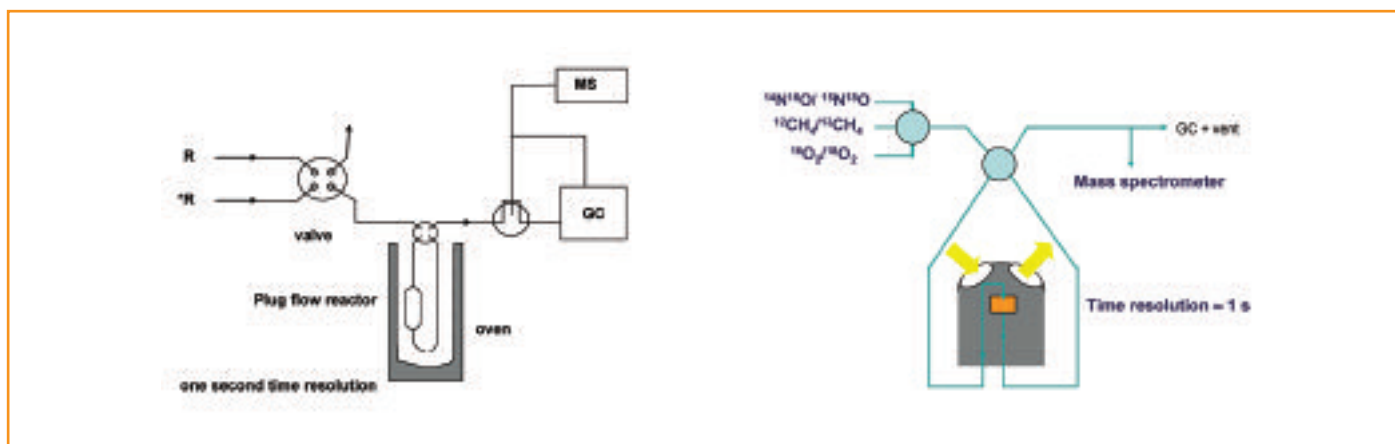


Fig. 1 - Schematic set-ups for SSITKA in plug flow (left hand side) and DRIFT (right hand side) reactors

labeled concentration both in the reactant, the pool of intermediate adspecies and the products contain all the kinetic information above mentioned, mean residence time and therefore surface concentration. Refs. [4-6] provide detailed mathematical description of SSITKA with curves modelling in plug flow reactor [23, 24]. Fig. 1 schematizes a SSITKA set-up for a plug-flow and for a DRIFT reactor.

Carbon monoxide hydrogenation into methane

Methanation over Ni/SiO₂ catalysts

As an example of using SSITKA for describing the steady state of a catalyst, the CO hydrogenation into methane was studied over a Ni/SiO₂ catalyst in order to understand the ageing process related to the kinetic behavior at steady-state [7]. The methanation reaction (feed H₂/CO = 2) was carried out in the 230-350 °C temperature range and at atmospheric pressure in a fixed bed flow reactor. The isotopic transient experiments under steady state conditions were carried out by changing rapidly the composition of the feeding mixture from ¹²CO + 2H₂ to ¹³CO + 2H₂ or from ¹²CO + 2H₂ to ¹²CO + 2D₂ and vice versa at the inlet of the micro reactor.

After an initial period of carbon deposition, fast sintering and particle smoothing via nickel carbonyl transfer, the reacting surface can be described as a monolayer of nickel carbide, largely covered by CO adspecies with an average bonding stoichiometry of CO/2Ni_s. The rate of hydrogenation is controlled by the probability for a hydrogen molecule to collide with an active site formed of one to two adjacent Ni atoms free from adsorbed CO. The concentration of active sites is statistically determined by the CO coverage. Carbon atoms belonging to the carbidic layer associated to the active site are hydrogenated by hydrogen activated on the free Ni atoms. The regeneration of the carbidic layer is in turn ensured by CO dissociation after methane desorption. The following rate equation was proposed with

physically meaningful kinetic parameters:

$$r = k_0 \exp(-E_0/RT) P_{H_2} (1-\theta_{CO})^{1.2}$$

where the true activation energy can be expressed as:

$$E_0 = E_a - E_{adspecies} = 22.1 - 6.7 = 15.4 \text{ kcal}$$

The true rate constant k_0 is:

$$k_0 = 4.4 \times 10^{18} \text{ molec./s cm}^2 \text{ Ni Torr.}$$

By comparing this value to the number of H₂ molecules colliding the nickel surface ($V = 1.1 \times 10^{21}$ collisions/s cm²_{Ni} Torr), a sticking coefficient of 1/250 can be derived.

This example demonstrates how a direct evaluation of coverages and therefore of true kinetic parameters may lead to a kinetic model which can be considered as a microkinetic model, without any fitted parameters.

Fischer-Tropsch (FT) synthesis

In continuation of the previous study, the use of SSITKA for analyzing an operating FT catalyst was attempted several times [8, 9] and recently by van Dijk *et al.* [25], reflecting a renewed interest for this process due to environmental constraints and demand for clean (sulfur free) and renewable (based of bio-carbon) synthetic fuels. Transient responses were recorded for alkanes (methane to butane),

and alcohols (methanol to propanol), each series of hydrocarbons or oxygenates being deconvoluted into isotopic distribution by using a 12-loops sampling valve on line with a GC-MS analysis. A general mechanism for FT synthesis was derived from this SSITKA investigation which assumes that i) one pool for C₁ carbene like adspecies establishes as Cα and Cβ (CO→Cα→Cβ) and one distinct pool establishes for C-C coupling, ii) higher alcohols are formed via CO insertion into carbene adspecies and iii) a physically adsorbed HC layer exists over the whole surface.

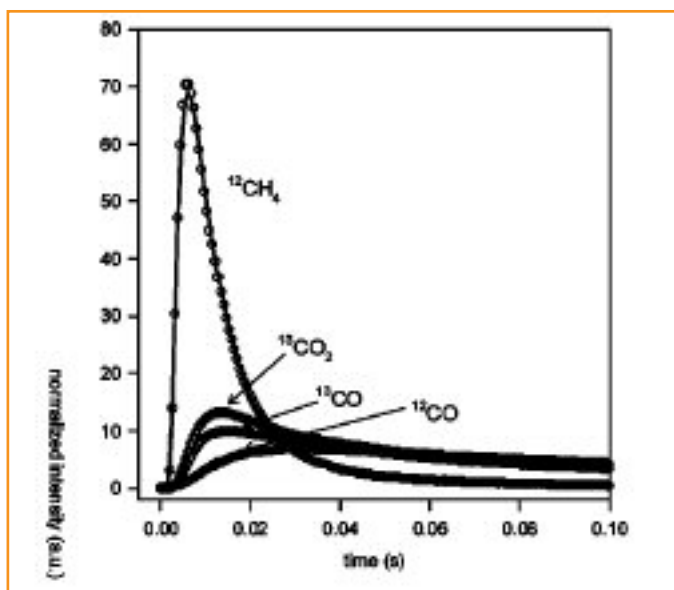


Fig. 2 - Experimental (symbols) and model (lines) TAP responses of methane, carbon dioxide and carbon monoxide on a pulse of ¹²CH₄+¹³CO₂ over Ni/SiO₂ at 600 °C [26]

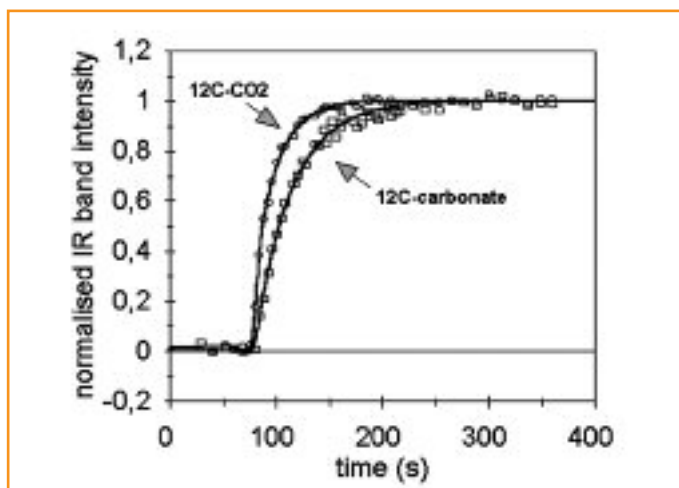


Fig. 3 - Transient SSITKA curves obtained on Ni/La₂O₃ from in situ DRIFT showing the changes in isotopic concentration of unlabelled CO₂ outlet gas and the changes in band intensity of the unlabelled steady-state carbonates (symmetrical curves for labelled species are omitted for sake of clarity) [27]

Note however that these experiments were always carried out at low pressure (~1 bar) since labelled gases necessary for SSITKA (¹³CO, C¹⁸O, D₂) are expensive and hardly delivered under high pressure.

Methane reforming by carbon dioxide (dry reforming)

This key reaction, close to the industrially prominent steam reforming, is related to the existence in most natural gas reserves of high amounts of carbon dioxide. The perspective of CO₂ recycling is also boosting fundamental studies for establishing a clear mechanism and a robust kinetic model aiming at optimizing existing processes. In [26], Pinaeva *et al.* review the main fundamental aspects of the dry reforming reaction focussing at the various carbon routes that determine the fate and performance of any nickel or noble metal based catalyst. They illustrate how transient kinetics, SSITKA and TAP, can be used appropriately for evaluating which accumulating carbon is “active” and which part is only stored without participating to the reaction (as filaments and/or amorphous graphite).

Thus, a general kinetic scheme was validated by modelling successfully transient responses obtained in the TAP reactor (fast pulsed reactor for Temporal Analysis of Products) for the formation of ¹²CO and ¹³CO from a mixture of CH₄ and ¹³CO₂ over Ni/SiO₂ at 600 °C as depicted in Fig. 2. It demonstrates the fast formation of ¹³CO from the dissociation of ¹³CO₂ and the slower formation of ¹²CO from the reaction of surface oxygen coming from CO₂ dissociation with surface ¹²C formed from methane dissociation. Indeed, the TAP responses can be adequately modeled on the basis of the reaction steps as discussed in [26].

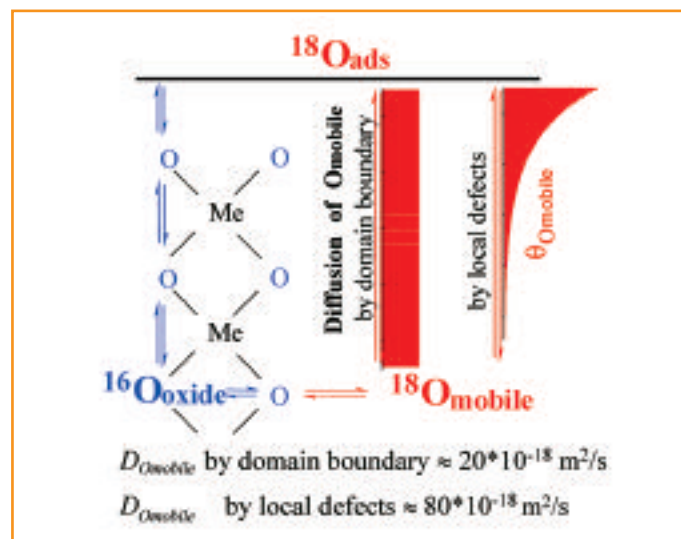


Fig. 4 - Various pathways for oxygen diffusion from bulk to surface

Besides the rapid steps which constitute the catalytic cycle, this pool of active carbon is shown to undergo slow side reactions which may lead to poisoning carbon accumulation.

In [27], Slagtern *et al.* investigate the unique stability of Ni/La₂O₃ system compared to reference systems like Ni/SiO₂. From SSITKA measurements performed in a DRIFT cell (Fig. 3), they deduce the existence of a tight interface between a lanthanum carbonate phase and the nickel particles which was perfectly confirmed by TEM. A “bi-functional” mechanism is proposed to account for the observed kinetic behaviour: methane is activated on the Ni particles, carbon dioxide interacts with La₂O₃ to form carbonates which scavenge carbon from nickel at the Ni-La₂O₃ interface, thus

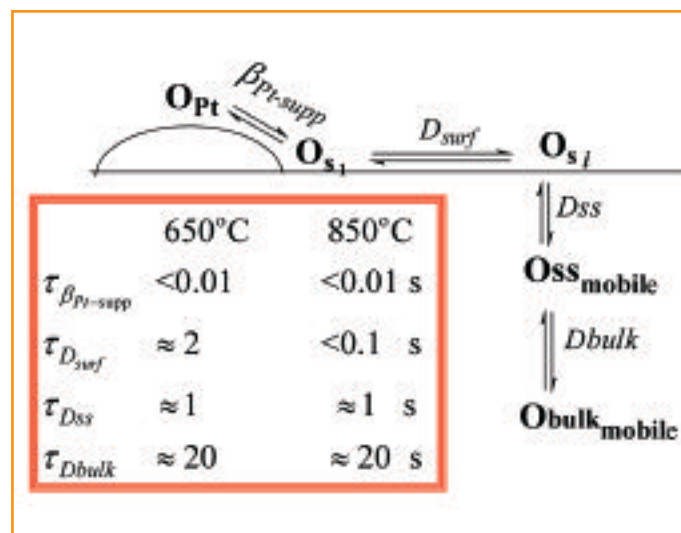


Fig. 5 - Scheme for oxygen surface and bulk diffusion and main characteristic times of diffusion determined from SSITKA curves modelling [15]

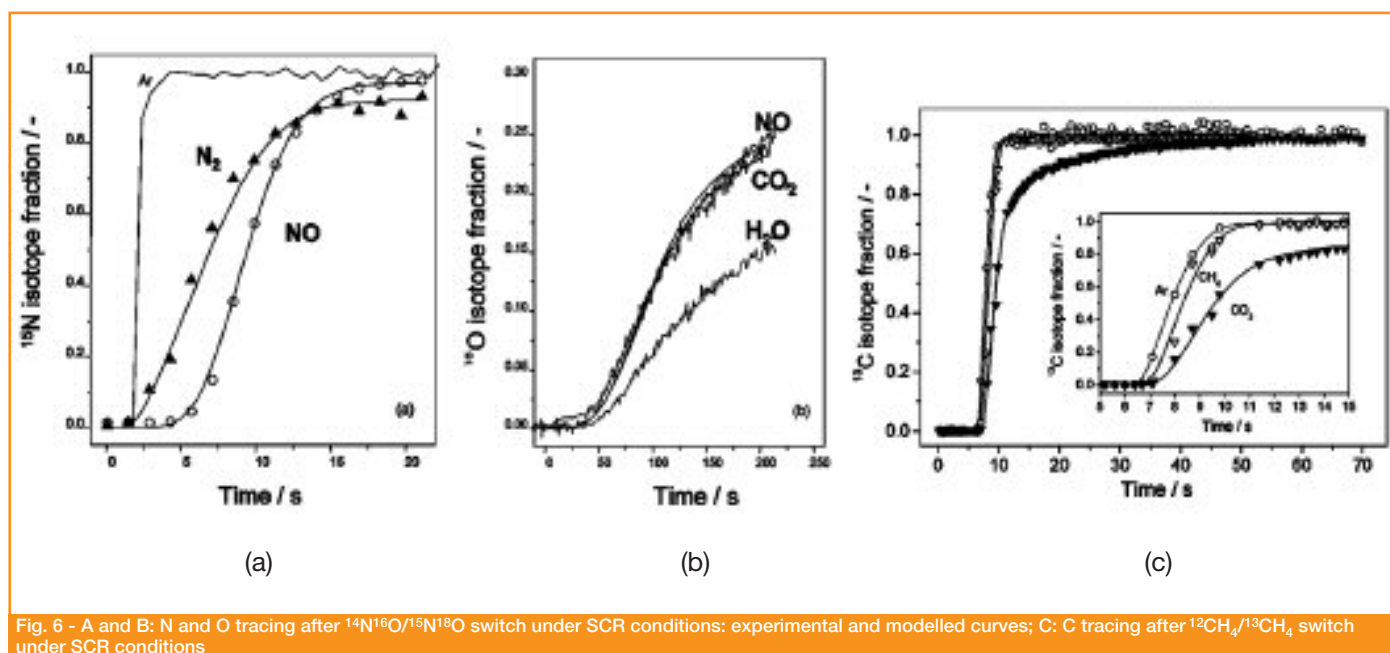


Fig. 6 - A and B: N and O tracing after $^{14}\text{N}^{16}\text{O}/^{15}\text{N}^{18}\text{O}$ switch under SCR conditions: experimental and modelled curves; C: C tracing after $^{12}\text{CH}_4/^{13}\text{CH}_4$ switch under SCR conditions

restoring the Ni particles to their original state. This specific morphology of the active phase is also assumed to hinder the formation of deactivating coke, which explains the outstanding catalytic stability of such a catalyst.

Methane partial oxidation over ceria-zirconia based systems

Alternative to the conventional steam reforming, the partial oxidation of methane (POM) might be implemented in short residence time reactors over noble metal grids or highly stable mixed oxides coating structured monoliths. A major question concerns the specific role of the support, and especially of the various oxygen species stored in or on the mixed oxide.

The SSITKA of $^{18}\text{O}/^{16}\text{O}$ isotopic exchange over $\text{CeO}_2\text{-ZrO}_2\text{-La}_2\text{O}_3$ and $\text{Pt/CeO}_2\text{-ZrO}_2$ catalysts have been investigated at 1 bar and 650-850 °C [15]. The nanocrystalline structure of lanthana doped ceria-zirconia prepared via the Pechini route is found to guarantee a high oxygen mobility in the oxide bulk leading to the accumulation of over-stoichiometric oxygen. For $\text{Pt/CeO}_2\text{-ZrO}_2$ oxygen transfer from Pt to support was shown to be responsible for the fast exchange between the gas phase oxygen and oxygen adsorbed on the mixed oxide surface. The rate of direct exchange between the gas phase and surface oxygen is increased as well, due to the increased concentration (up to 2 monolayers) of surface/near subsurface oxygen species accumulated on the oxygen vacancies (originated from the incorporation of highly dispersed Pt atoms).

Fig. 4 and 5 schematize the routes of oxygen diffusion from the bulk to the surface and the characteristic times measured from the curves simulation. The characteristic time of diffusion of the oxygen localized in the subsurface layers is about 1 s, while it reaches about 20 s within the bulk. All these kinetic data are required for the further step of modeling partial oxidation of hydrocarbons under steady- and unsteady-state conditions.

Selective catalytic reduction (SCR) of NO by CH_4 over Co-ZSM-5 catalysts

Despite numerous studies, the kinetic understanding of the selective reduction of NO with CH_4 in the presence of excess oxygen over Co-ZSM-5 is poor and often controversial. The nature and distribution of cobalt species have been characterized by XRD and EXAFS, showing that no bulk cobalt oxide exist but only oligonuclear clusters and isolated cobalt ions stabilized in the zeolite matrix. In situ temperature-programmed DRIFT studies in $\text{NO}+\text{O}_2$ mixtures performed from 393 to 723 K enable to identify four types of surface NO_x adspecies over Co-ZSM-5: cobalt dinitrosyls at 1,810 cm^{-1} observed at low temperature, mononitrosyls adsorbed on isolated Co-ions (at 1,930 cm^{-1}), nitrite and nitrate complexes adsorbed on the largest cobalt ions agglomerates (around 1,520 cm^{-1}) and stable $\text{NO}_2^{\delta+}$ species situated at the interface between cobalt species and hydroxyl groups from the zeolite lattice (at 2,130 cm^{-1}). $\text{NO}_2^{\delta+}$ species were found to be highly reactive intermediates in deNO_x $\text{CH}_4\text{-SCR}$ [28].

The elementary steps involved in the SCR of NO with CH_4 were

Surface coverage of Co phase in ZSM-5 with active species determined from SS kinetic models (A&B) and SSITKA

| | θ_o | θ_{OCH_3} | θ_{NO_x} | θ_{OH} | θ_{ONOOCH_3} | θ_{free} |
|----------------|------------|------------------|-----------------|---------------|---------------------|-----------------|
| Model A | 0.007 | 0.003 | 0.25 | 0.01 | 0.09 | 0.64 |
| Model B | 0.009 | 0.003 | 0.27 | 0.01 | 0.00 | 0.71 |
| SSITKA | 0.01 | 0.002 | 0.10 | 0.06 | 0.00 | 0.83 |

identified and quantified from the SSITKA switches: $^{14}N^{16}O \rightarrow ^{15}N^{18}O$, $^{16}O_2 \rightarrow ^{18}O_2$, and $^{12}CH_4 \rightarrow ^{13}CH_4$, as illustrated in Fig. 6A-C [28]. The reaction rates of the different forms of NO_x species with methane indicate that the reduction of NO with CH_4 proceeds by two different routes with participation of $NO_2^{\delta+}$ and nitrite complexes, the rate of the first route being appreciably higher. Mononitrosyls species appear not to be involved in the overall process, although they may participate upon conversion into nitrites.

A step further was to compare the surface coverages obtained from SSITKA to the ones obtained from a conventional kinetic analysis at steady-state (considering two distinct models A and B), as reported in [29]. As can be seen from the Table above, despite a clear converging trend in mean surface coverages, discrepancies still exist between the two approaches, likely due to the approxi-

mate definition of active sites for this case of oxide materials as compared to metallic surfaces.

Conclusions

SSITKA permits a quantitative evaluation of active and “spectators” species concentration but without indication on the chemical nature of these surface intermediates. In turn, in situ SSITKA DRIFT gives access to the nature of the most abundant adspecies. Despite converging coverage trends can be observed between SSITKA and stationary kinetics, some discrepancies are likely to be assigned to model discrimination and site nature definition issues.

As a perspective, these highly efficient isotope-based techniques carried out in single reactor should be expanded to high throughput SSITKA parallel reactors. A fast access to true kinetics would

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