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Steady-state and unsteady-state kinetic approaches for studying reactions over three-way natural gas vehicle catalysts[☆]

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ABSTRACT

Kinetics has been proven to be a powerful method to probe catalytic surfaces under reaction conditions in order to elucidate, at molecular level, complex chemical processes. Numerous techniques and methodologies have been already implemented (surface science approaches, TAP, SSITKA...) running in very different pressure ranges (*pressure gap*) which led to controversial statements regarding suggested mechanism schemes, especially for DeNO_x reactions. Two typical reactions taking place over NGV catalysts have been selected to illustrate which information can be tackled from kinetic measurements. Both reactions occur in different temperature ranges and are sensitive to the structure of the catalyst, to the surface composition of bimetallic particles, with possible surface enrichments, and to the participation of the support. Hence, it will be tentatively demonstrated that kinetic combined with spectroscopic or theoretical methods can be appropriate to establish relevant correlations between kinetic parameters and the topology of the catalyst surface.

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R É S U M É

L'étude cinétique permet de caractériser les propriétés d'une surface catalytique sous atmosphère réactionnelle et définir à l'échelle moléculaire les processus chimiques impliqués à la surface. Différentes méthodes d'analyse (sciences des surfaces, TAP, SSITKA...), prenant en compte des domaines de pression variant de plusieurs ordres de grandeur, ont parfois conduit à certaines controverses sur les mécanismes suggérés, notamment en catalyse DéNO_x. Deux réactions intervenant sur des catalyseurs de type GNV ont été sélectionnées, activées à différentes températures, et sensibles à la structure du catalyseur. Dans ce dernier cas, cette sensibilité peut être reliée à la composition de surface de catalyseurs bimétalliques. L'interface métal/support peut jouer également un rôle clé. Cette revue a pour objectif de montrer le potentiel de ces différentes approches pratiques, notamment lorsqu'elles sont combinées. L'étude cinétique en régime stationnaire ou transitoire associée à des techniques spectroscopiques en mode *in situ* ou aux calculs théoriques semble appropriée pour extraire des informations permettant d'établir des corrélations structure/réactivité pertinentes.

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[☆] Thematic issue dedicated to François Garin.

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1. Introduction

Kinetics plays a central role in catalysis and is not solely restricted to fundamental approaches providing new insight into reaction mechanisms. Indeed, recent investigations underlined the potential of kinetic modeling from a practical point of view [1]. For instance, the efficiency of lean NO_x trap systems can be optimized by using a microkinetic model [2,3] with the objective to lower the noble metal content. Hence, there is presently a growing interest to develop robust mathematical models for predicting unsteady-state kinetic regimes in order to control more efficiently integrated after-treatment systems [1,4,5]. Different methodologies have been already envisioned which consist in integrating kinetic parameters previously determined on powder catalysts in a numerical model adapted for the prediction of outlet gas composition of Selective Catalytic Reduction (SCR) monolith reactors. This strategy was profitably used to highlight the inhibiting effect of ammonia and to define the optimal surface coverage at low temperature. From this approach, it seems possible to implement intelligent urea dosage strategies for lean-burn after-treatment systems. Zuckerman et al. [1] used the COMSOL Package environment to create a platform capable to simulate the dynamic behavior of coupled NO_x storage/Reduction (NSR) and SCR after-treatment systems integrating separate kinetic models for ammonia formation and oxidation during the regenerative step of the NSR catalyst (Fig. 1). Based on these previous achievements, it seems obvious that such predictive mathematical tools can be adapted for more complex architectures of after-treatment systems combining Diesel oxidation catalysts (DOC), Diesel particulate filter (DPF), NO_x storage reduction (NSR) and selective catalytic reduction (SCR) systems including chemical processes at the surface of the catalyst and the effects of transport phenomena which affect the catalyst efficiency.

Returning to fundamental aspects, numerous investigations implemented kinetic approaches to a wide panel of

applications under steady-state [6–14] or transient operating conditions [15–17]. Further developments of new advanced methodologies such as Steady-State Isotopic Transient Kinetic Analysis (SSITKA) utilizing labeled molecules [18–23] also contributed to the elucidation of complex surface chemical processes. Parallel to those developments, surface science investigations provided in the past three decades reliable information on the nature of elementary steps especially in the field of environmental catalysis in connection with the development of Three-Way Catalysts (TWC) containing noble metals (Pd, Pt and Rh). While those experiments have been currently performed over model catalysts and under Ultra-High-Vacuum (UHV), far from realistic pressure conditions, they provided useful kinetic data related to the structure sensitivity of the reduction of NO over noble metals [24–27]. These results have been further verified over polycrystalline catalysts as reported elsewhere [28].

The emergence of new experimental techniques also contributes to a better nano description of the catalysts. First, the strategy associated with the implementation of the Temporal Analysis of Products (TAP) reactors [28–33] can be considered as an intermediate approach between classical kinetic and surface science studies, characterizing real catalysts rather than single crystals and in pressure ranges higher than those currently encountered in this latter case. Interestingly, it was found that the kinetic parameters obtained from TAP measurements can correctly model steady-state kinetic experiments at higher pressure conditions [34,35] emphasizing the fact that the strategies developed by using this technique can be considered at the boundary between conventional kinetics and surface sciences. The development of microkinetic approaches is also intimately related to the implementation of spectroscopic techniques that can probe the surface under reaction conditions. This approach is more reliable since the construction of active sites will strongly depend on the nature of the gas composition under reaction conditions initiating surface reconstructions which can

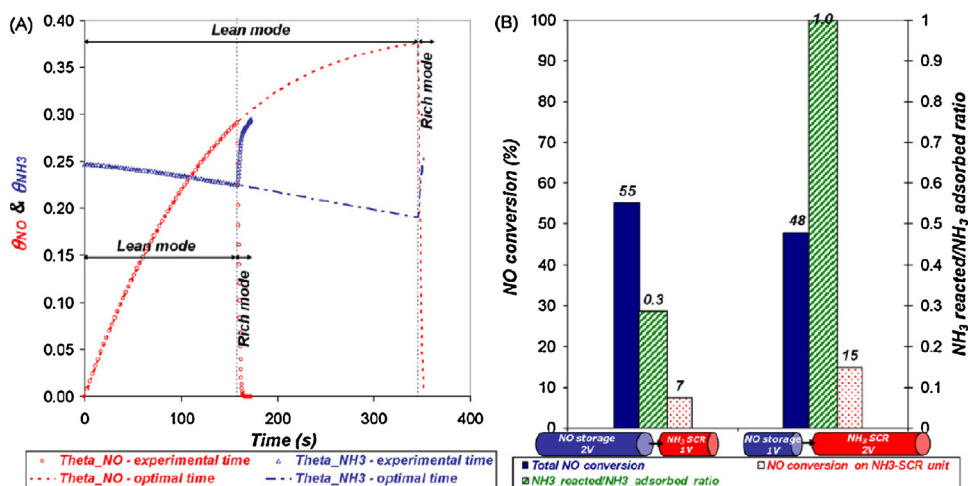


Fig. 1. (Color online.) A. θ_{NO} and θ_{NH_3} (the ratio between adsorbed NO and NH_3 to catalyst capacity, respectively) in NO_x storage unit and NH_3 -SCR unit, as a function of time (at experimental time and optimal time). B. NO Conversion and the ratio between reacted NH_3 and adsorbed (stored) NH_3 for two volume configurations. Reproduced with permission from reference [1].

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