



Microkinetic evaluation of normal and inverse kinetic isotope effects during methane steam reforming to synthesis gas over a Ni/NiAl₂O₄ model catalyst

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ABSTRACT

A microkinetic model was developed and applied to simulate an extensive experimental dataset on methane steam reforming. The data set consisted of 537 data points, and was collected over a Ni/NiAl₂O₄ catalyst at 843, 858, and 873 K in a wide steam-to-carbon ratio range between 0.2 and 7.1. A microkinetic engine modeling tool was applied for the construction and parameter estimation of an elementary step network consisting of 12 reversible reactions. Specific reaction pathways were implemented for the formation of CO and CO₂, respectively. The model qualitatively if not quantitatively explains inverse and normal isotope effects experimentally observed at low and high S/C ratios, respectively, and is thermodynamically consistent. A combination of the approach to partial equilibrium (i.e. whether the elementary step proceeds forward or backward) and net rate (i.e. the difference between forward and backward reaction rate) provides novel insight into the oxidation mechanism of CH_x and CH_xO surface species.

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1. Introduction

Natural gas is an important source in the global energy supply chain [1]. Methane, the major component in natural gas, is, furthermore, utilised for the production of valuable chemicals via its conversion to synthesis gas (also denoted as syngas, a CO/H₂ mixture) [2], which is then further processed. The most important products out of natural gas are methanol and pure hydrogen, with ammonia representing a further important downstream derivative [3].

Methane steam reforming (MSR) over nickel catalysts is a major process for syngas production, and especially pure hydrogen production [2,3]. Early investigations on the kinetics of the MSR process were based on simple kinetic models. Gaseous molecules were assumed to react with adsorbed surface species upon collision [4–6]. Further developments incorporated the adsorption of all reactants and products [7,8]. Empirical rate equations were derived and gave a satisfactory description of the investigated experimental conditions [9].

Additionally, the concentration of species on the catalyst surface was incorporated in the rate expression [10–12], and its physical

meaning was validated. Adsorption coefficients and corresponding enthalpies were estimated and compared to values derived from experimental methods. Such Langmuir–Hinshelwood approaches were based on elementary step models, in which one or several kinetically relevant steps are assumed. The respective rate expressions were derived accordingly. Due to the presence of reactant partial pressures in the numerator and, also, the denominator, the dependence of the reaction rate on a specific reactant partial pressure may be non-monotonic. These rate expressions [5,6,10–13] describe experimental observations in a broader range of operating conditions [14], and are, therefore, preferred in industrial applications.

The kinetic picture of methane steam reforming taken from the reported work in the last two paragraphs may be divided into two main categories, i.e., one where the methane adsorption [7,9,13,15], and a second one where an oxidation reaction on the surface [5,10–14,16], respectively, was assumed to be rate determining. The former statement was supported from isotopic labelling investigation on Ni/MgO catalysts, where methane adsorption was found to be irreversible [9]. In contrast to that, pulse experiments under vacuum conditions for nickel on different supports could show the fast adsorption of methane [17,18]. Investigations reported for a Ni/Al₂O₃ catalyst show that isotope effects depend on the reaction conditions [19].

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Further insight into mechanistic features was provided by microkinetic modelling and DFT calculations. The former approaches do assume an elementary step model, however, without considering a rate-determining step. Both experimental and theoretical data are accounted for [20–23]. The estimated activation energies and simulated concentrations of reaction intermediates offer valuable information about possible reaction pathways and the reaction rates. Kinetically relevant elementary steps as identified in literature models were the methane adsorption and dehydrogenation [20,23,24], and the C–O and OC–O bond formation [20]. Thus, it is possible and even likely that more than one step is significantly affecting the overall rate, when the experimental observations have been performed in a broad range of operating conditions. Such microkinetic models simulate the experimental data rather well in terms of reactant conversions and product selectivity [20,21,23–26].

More details on reaction pathways can be achieved from DFT calculations. Thermochemical characteristics of the surface intermediates were determined and, hence, allowed interpretations based on the free energy, which incorporates entropic effects. In accord with the categorisation mentioned above, CH₄ dissociation [24,27] and an oxidation reaction of C* [27,28], and CH* [24,28], respectively, may serve as a rate-determining step. It has been found that the temperature has a significant effect on which step could eventually be rate-determining [27,28], and which intermediate is part of the main reaction pathway for the oxidation reaction (C* or CH*) [28]. In a site dependent investigation by Blaylock et al. [28] generally higher binding and adsorption energies were predicted on the step edges Ni(2 1 1), in comparison to the Ni(1 1 1) and Ni(1 0 0) facets. Hence, the reaction pathways differ for various sites on Ni surfaces. Even though DFT calculations give valuable insight into the mechanism, a main challenge remains to describe experimental data quantitatively.

In this investigation we employ a microkinetic modelling approach to describe the experimental data provided in Sprung et al. [29]. Both reactants were found to affect the methane conversion rate [29,30]. The partial reaction orders of steam and methane varied from zero, or even negative for steam, to one, depending on the S/C applied. Based on the partial reaction orders of the reactants, two kinetic regimes were distinguished. At low S/C the kinetics were determined by high steam and low methane partial reaction orders, whereas the situation was inverse at high S/C. Switch experiments under steady state conditions between CH₄ and CD₄ feed revealed kinetic isotope effects (KIE – ratio of methane conversion at CH₄/H₂O to CD₄/H₂O feed, i.e., χ_H/χ_D). This effect was inverse (i.e., <1) at low S/C, and normal (i.e., >1) for experiments under high S/C conditions.

The isotope effect caused by the hydrogen isotopes is the most pronounced due to their relative mass difference (deuterium (D), and tritium (T) are two-, and threefold, respectively, the mass of protium (H)). Such a mass difference has remarkable influence on the chemical bond between two atoms, especially their vibrational levels. Details on the origin of isotope effects are found in the literature in this field [31,32]. The cleavage of a C–H requires less energy compared to a C–D bond. The isotope effect in that case is *normal*, i.e., >1 due to a faster reaction for C–H than C–D bond cleavage [31,32]. An *inverse* isotope effect is, in contrast to the *normal* effect, not caused by a bond cleavage process, and is in general of minor magnitude compared to the former. An overview on the possible origins of an *inverse* isotope effect with focus on methane steam reforming was given in Ref. [29], and shall not be repeated here. It was concluded that the origin is most likely a hybridisation change towards more p-like orbitals (i.e., $sp^2 \rightarrow sp^3$, for which an isotope effect of 0.8–0.9 is expected [32]). Hence, the C–H/C–D bond has to stay intact at the carbon atom, which takes part in the reaction.

In conclusion, the occurrence of both an inverse and a normal isotope effect at low and high S/C, respectively, suggests that two different reaction pathways are kinetically relevant: i.e., one where the C–H bond stays intact and a second one where this bond is cleaved.

Isotope effects were so far introduced in connection to kinetics, i.e., in the way the experiments have been carried out [29]. The thermodynamic isotope effect (TIE) is defined as the ratio of equilibrium coefficients, i.e., K_H/K_D [31,33]. Kiperman proposed a concept in which an observed isotope effect is composed of both a kinetic and a thermodynamic isotope effect [34]. An overall normal TIE was observed for methane steam reforming under thermodynamic equilibrium conditions, however an inverse isotope effect on the methane conversion was simulated for low S/C ratios [35]. We want to widen the field of view in this topic, and also consider equilibrium/thermodynamic isotope effects for surface reactions in partial equilibrium.

In summary the two kinetic regimes distinguished by the categorised partial reaction orders of the reactants [29,30] and the observed kinetic isotope effects [29] discard the assumption of a single reaction step determining the rate of the overall reaction in the investigated S/C range. A microkinetic modelling approach was, therefore, considered. The mechanistic features of the model established by Xu and Froment [11] were used as a basis for the developed microkinetic model, however in contrast to the approach of the latter authors, no rate-determining step was assumed in the current work. Hence, it was possible to identify and evaluate all kinetically relevant reaction steps at the wide range of studied conditions. The final elementary step model with 12 reversible reactions was developed on the basis of the experimental observations reported in [29,30].

2. Catalyst and experimental procedure

A brief summary of the catalyst synthesis and experimental procedure will be given here. Further details on catalyst synthesis, characterisation, the experimental equipment and the catalytic testing procedure are reported by Sprung et al. [29,30,35].

The catalyst was a 2 wt% NiO/NiAl₂O₄. A water/*i*-propanol solution of nickel nitrate and aluminum nitrate was dried and the solid precursor calcined at 1473 K in static air. The catalyst, diluted with α -Al₂O₃ (1:50, 250–420 μ m, total catalyst bed mass 500 mg), was placed inside an alumina fixed bed tubular reactor. Gas flows were controlled by an array of mass flow controllers. Steam was provided by a two stage steam generator set-up, where an Ar gas stream was flushed through water at elevated temperatures. Two MicroGC's (Agilent 3000) analyzed simultaneously reactant and product gases.

After activation in 10 vol% H₂/Ar at 873 K the catalyst was stabilized at 873 K and reference conditions (6.3% CH₄, 12.3% H₂O in Ar, $W/F_{CH_4} = 1.224 \text{ kg}_{cat} \text{ s mol}_{CH_4}^{-1}$) before performing partial pressure variation experiments at a total flow rate of 200 Sml min⁻¹. The catalyst deactivation was traced by a segment under reference conditions after each partial pressure variation segment, both lasting for 30 min. The data were corrected for deactivation by the trace of methane conversion under reference conditions. All product and reactant streams were corrected by assuming the determined carbon, hydrogen, and oxygen balances, and the CO₂ selectivity to be equal for the raw and corrected data. Details on how these corrections were performed are found elsewhere [29].

This partial pressure variation was performed at three temperatures (i.e., 843, 858, and 873 K) in a steam-to-carbon ratio (S/C) range of 0.2–7.1, and incorporates in total 537 data points.

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