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Low temperature steam reforming of methane: A combined isotopic and microkinetic study

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A B S T R A C T

Low temperature steam reforming in combination with hydrogen selective membranes presents great potential of intensifying the classical industrial hydrogen production process via natural gas. This concept can lead to significant environmental and process benefits, such as reduced energy needs, milder material stability requirements and considerably simplified process layouts via e.g. avoiding the use of downstream WGS reactors. Ni and Rh based catalysts supported on La_2O_3-CeO_2-ZrO_2, already identified as active and stable at these conditions, are further investigated in the current work aiming at the elucidation of reaction kinetics. Temperature programmed experiments of methane conversion in steam reforming and decomposition modes in conjunction with isotopic investigations using CD_4 are carried out, showing that cleavage of a C—H bond participates in the rate determine step, whereas steam derived intermediates do not. A thermodynamically consistent microkinetic model considering a comprehensive set of surface pathways is also developed. The model describes correctly experimental trends, predicting surface CH_3 dehydrogenation to be rate limiting. Estimated model parameters further help elucidate the different catalysts' activities. The combined approach presented shows potential to accelerate catalyst and process design efforts for the promising low temperature steam reforming hydrogen production process.

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1. Introduction

Hydrogen presents significant potential as an energy carrier that can drive the implementation of efficient and environmentally benign energy systems. Industrial hydrogen production via natural gas steam reforming is accompanied, though, by significant CO_x emissions from the burner supplying heat to the endothermic reaction. The need for intensification of the process has spurred the search for alternative concepts, with methane steam reforming (MSR) at a low temperature range of 400–550 °C being one such promising approach. The milder operating conditions lead to lower operation and materials costs, while the favorable temperature eliminates the need for separate water gas shift reactors. Thermodynamic limitations, resulting in low CH_4 conversions and H_2 yields, can be surpassed using selective membranes that remove hydrogen *in situ*. As a result, hydrogen is separated with high purity and at the same time the reforming reaction equilibrium is shifted to the product side [1,2].

The use of highly active and coke resistant catalysts at these low temperatures is a key factor to the success of such a system. Ni-based catalysts combine good activity and low cost [3,4], whereas noble metal ones, although typically of higher activity than Ni, are limited by their high cost [5]. The support type can also contribute to the properties of an ideal reforming catalyst [3]. Reducible supports such as CeO_2 and CeO_2–ZrO_2 mixed oxides are good candidates for low temperature MSR due to their active role in the redox mechanism through the mobility of surface oxygen species [6–13]. Addition of La [14] can further improve the oxygen storage capacity of CeO_2–ZrO_2, enhancing both the coke resistance [15,16], and thermal stability of the catalyst [17].

A series of Ni and Rh catalysts supported on lanthana and/or ceria modified zirconia were prepared and evaluated for their performance in low temperature steam reforming [18,19], showing high activity at the 400–550 °C region and close to equilibrium CH_4 conversion at relatively short contact times. The notably stable behavior of both metals supported on lanthana doped ceria-zirconia during model biogas steam reforming at ambient pressure highlighted the importance of CeO_2 in the support. The Ni-based catalyst, especially, performed remarkably at extended high pressure 90-h-stability tests of model biogas steam reforming, showing

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minimal amount of carbon formation (0.05 wt%). The low coking tendency and resistance to sintering effects over both metals were ascribed to the active oxygen species provided by ceria and the thermal stabilization effect and low coking affinity of lanthana. TPO and TPH analysis of the carbonaceous deposits showed that the dominating type of carbon is highly reactive and can be easily removed by oxidation or hydrogenation at 500–550 °C. Analysis of these deposits at different reaction times showed a stable carbon amount with time on stream, implying that at least part of it is an active reaction intermediate.

As recently reviewed [6], the kinetics of MSR have been the subject of numerous studies. Wei and Iglesia [20–25] concluded to a comprehensive mechanistic picture for CH_4 activation in the presence or absence of any co-reactant (CO_2, H_2O) on Ni- and various noble metal-based catalysts. Identical forward CH_4 reaction rates, rate constants, kinetic isotope effects, and activation energies were measured, with CH_4 rates found to be limited solely by C—H bond activation and unaffected by the identity or concentration of co-reactants. Nørskov and coworkers [26], combining first-principles calculations and experimental investigations on pure transition metals, determined a CH_4 dissociation and a CO formation step to be kinetically limiting, with the latter dominating at lower temperatures. Vlachos et al. have notably developed an elaborate microkinetic model, based on semi-empirical and first principle techniques [27,28], able to describe CH_4 steam and dry reforming over Rh catalysts [29,30]. For both reactions, CH_4 activation was found to be rate-determining [29], in agreement with Wei and Iglesia [21]. Deutschmann et al. have presented a multi-step microkinetic model also describing both reforming reactions over Ni catalysts [31,32], however a sensitivity to oxidative dehydrogenation indicated the kinetic relevance of steam in MSR. Chen et al. [33,34] in their microkinetic model over Ni, interestingly, accounted also for filamentous carbon formation. Blaylock et al. initially developed a microkinetic model based on DFT-calculated Ni(111) thermochemical data [35] that was further extended via calculations on Ni(100) and Ni(211) surfaces to improve the description of data on multifaceted Ni catalysts [36]. The same approach for CH_4 dry reforming was recently considered in the work of Fan et al. [37].

In the current work a combination of temperature-programmed experimental techniques, isotopic studies and comprehensive microkinetic modelling is presented, aiming at obtaining insight on the kinetics of low temperature MSR over the promising La_2O_3-CeO_2-ZrO_2 supported Ni and Rh catalysts.

2. Procedures

2.1. Experimental

2.1.1. Catalyst preparation and characterization

The catalysts were prepared via the wet impregnation method using $Ni(NO_3)_2 \cdot 6H_2O$ (Merck) and $RhCl_3 \cdot 3H_2O$ (Pressure Chemical) as active metal precursors and lanthanum doped cerium – zirconium oxide (78 wt% ZrO_2, 17 wt% CeO_2, 5 wt% La_2O_3, Mel Chemicals) as catalyst support. In the following, the catalysts are referred to as M(x)CeZrLa, where M is the active metal and x the metal loading wt%. The surface area of the prepared materials was measured by N_2 adsorption at 77 K, using the multipoint BET analysis method (Autosorb-1 Quantachrome). X-ray diffraction (XRD) patterns were obtained using a Siemens D500 diffractometer, with Cu K_α radiation. The reducibility of the catalysts and the metal dispersion were investigated through temperature programmed reduction and desorption respectively. Further details on the experimental equipment, catalytic testing procedures and elaborate characterization have been reported elsewhere [19].

2.1.2. Catalyst testing and mechanistic experiments

The activity towards the conversion was tested at the temperature range of 400–550 °C at atmospheric pressure and methane partial pressure of 0.25–0.5 (H_2O/CH_4 ratio of 1–3). The data-set collected consisted of 54 experimental points. The laboratory unit is equipped with a mass flow-controlled system for gases admission, an UFLC pump (Shimadju) for the feeding of water to the reactor through a preheated line, a fixed bed quartz reactor, and an online gas chromatograph. Fresh catalyst powder was used in each test in order to avoid deactivation effects. In each test the GHSV was kept constant, while the temperature was decreased stepwise after equilibration of the system conditions [19]. The absence of external and internal mass transport limitations during the catalytic tests was ensured through the evaluation of criteria proposed by Mears [38] and Weisz-Prater [39], respectively.

In order to gain information on the main reaction pathways and explore the existence of Kinetic Isotope Effects (KIE), a series of temperature programmed experiments were performed in a gas flow system using a U-tube reactor. The catalyst sample (20 mg) was placed in the reactor and reduced for 1 h at 550 °C in 20% H_2/He. The temperature was then raised from ambient to 650 °C at a rate of 10 °C/min under the reaction mixture (50 mL/min). Tests with deuterated methane (CortecNet, 99% atom enrichment) were also conducted over the Ni and Rh catalysts. For all runs the reactor exit was monitored online with a quadrupole mass analyzer (Omnistar) by following the m/z signals: He: 4, H_2: 2, D_2: 4, CH_4: 16, CD_4: 20, CO: 28 and CO_2: 44. Overlapping fragments contributions on various gas compounds were taken into account. In order to avoid reoxidation of the reduced catalyst by the steam, the reaction mixture was in by-pass mode until the temperature of 350 °C for Ni-based catalyst and 250 °C for Rh-based catalyst. In temperature programmed methane decomposition experiments, the reaction mixture was 1.7% CH_4 (or CD_4) in He and Ar. For the steam reforming reaction, the reaction mixture consisted of 1.7% CH_4 (or CD_4) and 5.1% H_2O (S/C = 3) or 3.4% H_2O (S/C = 2) using as dilution gas He and Ar. To ensure that CD_4 concentrations measured are not affected by the formation of D_2O, contributing also at m/z = 20, CD_4 consumption rates were also calculated using the CD signal at m/z = 14 with the appropriate coefficient between masses at 20 and 14 accounted for. This ratio was calculated based on separate tests using a flow of pure CD_4 to the mass analyzer. Identical consumption rates were measured suggesting that exchange side reactions with H_2O and D species are not important under the experimental conditions applied. As above, standard criteria were applied to ensure measurements were conducted under explicit kinetic control and were unaffected by transport limitations, while multiple tests were carried out at the same conditions to verify the repeatability of results.

2.2. Modelling

2.2.1. Model formulation and computation details

The microkinetic model presented in this work has been developed with a FORTRAN-based (micro) kinetic modeling platform, the microkinetic engine (MKE), previously described in Metaxas et al. [40] and further used in Sprung et al. [41]. As experimental data have been collected under explicit kinetic control (see Ref. [19] and Section 2.1.2), a plug flow reactor model is used for the simulation of experiments. Furthermore, the pseudo-steady state approximation is made for the surface intermediates, accounting explicitly for the mass balance of the catalyst active sites. The DASPK 2.0 solver [42,43] is used for the solution of the above differential and algebraic equations system, while the Rosenbrock [44] and Levenberg–Marquardt [45,46] optimization methods are used for estimation of the model's parameters, namely chemisorption enthalpies and sticking coefficients. The latter can account for the