

TAP (Temporal Analysis of Products) studies of the catalytic conversion of biogas to syngas over Ni/SiO₂ catalysts

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TAP reactor, a unique transient technique, was used to study the mechanism of the conversion of biogas to syngas over a newly-developed Ni/SiO₂ mesoporous catalyst. Single-pulse, alternating pulse, and multipulse TAP experiments were performed at increasing temperatures, from RT to 600°C. Important conclusions about diffusion within the mesoporous catalyst, adsorption of reactant species at the surface of the catalyst, reaction and desorption of reaction products along with the type and lifetime of the intermediate species involved, were achievable through a qualitative and semi-quantitative analysis of the experimental TAP data.

These findings will be used to propose an optimal catalysts' formulation for the dry reforming reaction of methane with carbon dioxide.

1. Introduction

Recent global energy deficiency and more severe emission regulations, especially for CO₂, have motivated worldwide research on valorisation of biomass as a source of renewable energy and fuels. Beside direct combustion, the fermentation of carbohydrates to ethanol or 1st generation of biofuels, the fermentation of lignocellulosic feedstock to 2nd generation of biofuels, the cultivation of oil seeds for biodiesel, and the generation of biogas *via* anaerobic digestion were considered. We have concentrated our research on the anaerobic digestion of biomass and further on the catalytic conversion of biogas to syngas or "green gas" through the dry reforming of methane followed by a Fischer-Tropsch (FT) transformation to synoil.

This paper reports the results obtained so far on the mechanistic studies of the catalytic conversion of biogas to syngas over a newly-developed mesoporous Ni/SiO₂ catalyst, using a unique transient technique, the TAP reactor.

A TAP reactor system is a quite new but powerful experimental technique, introduced in 1986-1988, to study the kinetics and the mechanism of heterogeneous catalytic reactions by a pulsed transient response technique with sub millisecond time resolution

(Gleaves *et al.* 1988). The high time-resolution of the TAP reactor system is achieved by the use of high-speed pulse valves, a near zero dead volume manifold, and a catalytic micro-reactor placed directly inside a high-vacuum mass spectrometer detection chamber. In the TAP system an extremely narrow gas pulse is injected into the end of a cylindrical micro-reactor, while the other end is continuously evacuated. No carrier gas is used. The pulse moves across the micro-reactor as a result of the pressure gradient. The reactor is operated in a Knudsen diffusion regime in which transport is well defined. In the Knudsen regime the product pulse shape is independent of pulse-intensity. Therefore, Knudsen diffusion can be used and it is used as a “measuring stick” for extracting kinetic information. Although the TAP experiment can provide qualitative, semi-quantitative and quantitative information, respectively, the objective of this work was the analysis of the qualitative and semi-quantitative information only. Qualitative information allows us to obtain insights into the reaction mechanism. Using the TAP experiment, it is possible to detect short-lived intermediate substances that are released by the catalyst surface into the gas phase and, then, reveal information about various elementary steps of the complex catalytic reaction, i.e. diffusion, adsorption, surface reactions and desorption. To obtain qualitative information, single-pulse, pump-probe, and multipulse TAP experiments were performed. As for semi-quantitative information (Van der Linde *et al.* 1997), this consists of quantifying the adsorbed amount of certain species on the catalyst surface based on a procedure proposed by Gleaves *et al.* (1988). In the TAP experiments, the observed quantities are the outlet flows of gas molecules and related integral quantities, e.g., moments. The zeroth moment represents the total amount of gas molecules that emerges from the reactor, and the ratio of the first and the zeroth moments represents the average residence time of gas molecules in the reactor.

2. Experimental

All experiments were conducted using the TAP reactor system available at The University of Tokyo. Briefly, the apparatus consists of a catalytic micro-reactor, a gas delivery system for introduction of either high-speed gas pulses or a continuous flow of gas, a high-throughput, a high vacuum system and a computer-controlled quadrupole mass spectrometer. The micro-reactor is made from a quartz tube whose diameter and length are 2 mm and 25 mm, respectively. 0.0125 g of catalyst particles (250–425 μm) was loaded to and kept in the reactor by quartz wool. The length of the catalyst bed was about 10 mm. The reactor can be heated up to 773 K by cartridge heaters. The two high-speed pulse valves can be operated at the interval up to 50 pulses per second. The minimum pulse width is 200 μs . The pulse intensities were around 10^{15} molecule/pulse. The signal-to-noise ratio in the response was very high; therefore no averaging of a train of pulses was necessary.

The catalyst, a 5 wt% Ni on mesoporous silica, was prepared by multistep impregnation of Nickel acetate tetrahydrate onto the support, while the support, SBA 15, was prepared by sol-gel method (Gonzalez *et al.* 1997).

3. Results and discussion

3.1. Ar pulsing

Single-pulse TAP experiments with increasing Ar pulse intensities were performed at RT, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, and 600°C, respectively, to assess the diffusion behaviour. The zeroth moments were calculated and then, the Ar response curves were area normalized (results not shown). A unique diffusion curve was obtained for each temperature, for pulse intensities lower than 10^{16} molecule/pulse, which pointed out Knudsen diffusion as the only transport mechanism of the gases

through the bed (interparticle diffusion) and inside of the particles (intraparticle diffusion) as well. This was an important result taking into account the fact that our catalyst was a mesoporous one, with an average pore size of 5 nm. The intrapellet diffusion has an effect on the height and position of the peak of the measured pulse responses. When the area normalized Ar response curves were compared with those obtained with the same TAP set-up but over of a non-porous catalysts (same amount loaded to the reactor), with the same particle size, and at the same temperatures, the height of the peak over the mesoporous catalyst was always lower than that for the non-porous catalyst and the peak always appeared later. As for example, at RT the time difference was about 300 ms, getting smaller with increasing the temperature. However, the residence time of Ar over the porous catalyst at RT was only 30 ms higher than over the non-porous catalyst, i.e. 836 ms against 806 ms. As the characteristic times for diffusion on the bed and pellet scale have the same order of magnitude, the effective Knudsen diffusivity in the pellet pores has to be taken into account in the interpretation of a single-pulse TAP experiment. Using the residence time equation proposed by Zou *et al.* (1994), the effective Knudsen diffusivity in the porous catalytic bed was determined to be between $0.047 \text{ cm}^2/\text{s}$ and $0.072 \text{ cm}^2/\text{s}$, within the temperature interval considered for the experiments. The porosity of the bed was 0.23, the pellet porosity was 0.39, while the average Knudsen diffusivity for non-porous catalyst was $0.14 \text{ cm}^2/\text{s}$. Single-pulse TAP experiments with Ar were performed as well to check if different treatments of the catalyst's surface influence the diffusion behaviour. As seen in Figure 1, no difference between diffusion through a bed of fresh catalyst and a re-oxidized one was observed.

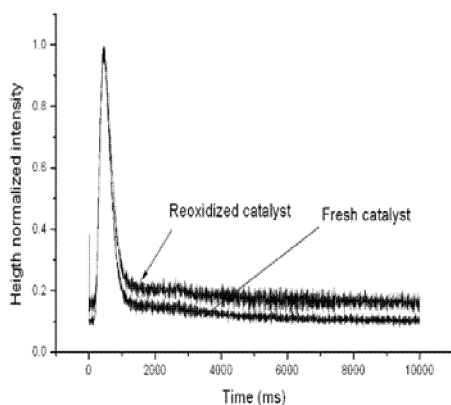


Fig. 1. Ar response curves at RT, over 0.0125 g of fresh and re-oxidized catalyst, respectively.

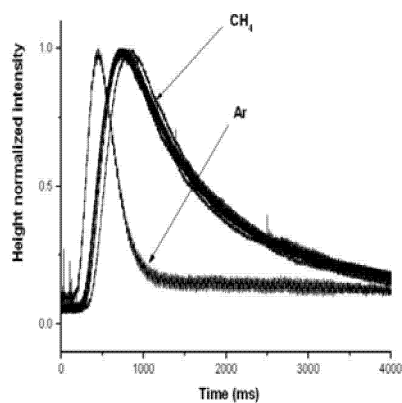


Fig.2. CH_4 response curves against Ar curve at increasing temperatures from RT to 600°C over 0.0125 g of fresh catalyst.

3.2. Methane pulsing

Single-pulse TAP experiments with a $\text{CH}_4:\text{Ar} = 5:1$ mixture were performed at the same temperatures as mentioned above. The CH_4 height normalized response was then compared with the Ar one. As shown in Figure 2, the CH_4 response was broader than the Ar one at all temperatures. By increasing the temperature, however, the CH_4 response curves shift to shorter time and slightly narrow. Small but increasing amounts

of H_2 were detected at the reactor exit for temperatures higher than $450^\circ C$. This is clear evidence that CH_4 undergoes a rather slow decomposition reaction over the catalyst through an irreversible adsorption. Along H_2 , carbonaceous species are formed on the surface as confirmed by the formation of CO_2 during the re-oxidation process, at temperature higher than $200^\circ C$.

3.3. Oxygen pulsing

Prior to the oxygen pulses the catalyst surface was treated at $600^\circ C$ with CH_4 multipulses until no changes in the CH_4 response were observed. Figure 3 shows the O_2 response curves measured after a number of 1, 20, 50, 100, and 400 pulses, respectively, were sent to the catalyst. No difference in the O_2 response was observed when the catalyst was treated with 300 or 400 O_2 pulses. It is obviously that the catalysts surface was reduced while being treated with CH_4 multipulses and the fact that O_2 sent over is able to reoxidize the surface, as the response curves show more than more O_2 leaving the reactor as the number of O_2 pulses increases. A CH_4 single pulse was sent over the reoxidized catalyst surface and the response was then compared with the one over the fresh catalyst. As no differences were observed we conclude that the reduction-reoxidation is a reversible process.

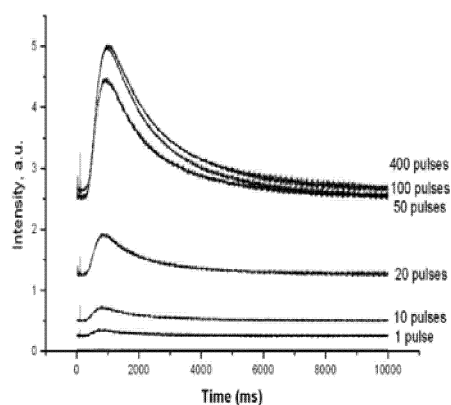


Fig.3. Oxygen response curves to increased number of O_2 pulses sent at $600^\circ C$ over 0.0125 g catalyst prior treated with CH_4 multipulses.

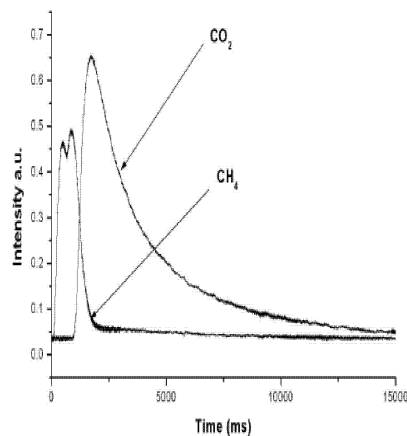


Fig.4. CH_4 and CO_2 responses at $550^\circ C$ with 500 ms delay between the two pulses.

3.4. Carbon dioxide pulsing

In order to check the adsorption behavior, single-pulse experiments with a $CO_2:Ar=5:1$ mixture were performed at the same temperatures as for the other experiments, over a completely oxidized surface of the catalyst. The qualitative analysis of the CO_2 response curves evidenced broaden curves for CO_2 with long tails at all temperatures (results not shown). No reaction products were detected. In our opinion, these results support a slow diffusion of CH_4 along with a weak adsorption through the catalyst bed.

3.5. Alternating pulse experiments with CH₄ as pump molecule and CO₂ as probe molecule

Two pulses were sent to the reactor. CH₄ was pulsed first to the surface, and then was probed by CO₂ pulses at different time intervals, from 50 ms to 5000 ms. As shown in Fig. 4, at 550°C and for a time interval of 500 ms, CH₄ seems to be adsorbed on two different active sites: one from which it desorbs quite easy, and another one from which it is forced to desorb as CO₂ competes as well for that adsorption site. Similar behavior was noticed at all temperatures and for all time intervals between the two pulses.

In addition, the response curves of CO₂ for all time intervals were compared at 600°C and it was found that the amount of unconverted CO₂ leaving the reactor decreases with increasing the time interval from 50 ms to 2000 ms. For time intervals higher than 2000 ms, the amount of unconverted CO₂ starts to increase, as seen in Fig. 5. In our opinion this happens because the pre-adsorbed CH₄ species on the surface have a limited lifetime of about 2000 ms. Therefore, by increasing the time interval between the two pulses at values higher than 2000 ms, less CH₄ is still on the surface, able to react with CO₂.

3.6. Alternating pulse experiments with CO₂ as pump molecule and CH₄ as probe molecule

Alternative pulse experiments with CO₂ as pump molecule were performed as well, at the same temperatures and same time intervals between the CO₂ and CH₄ pulses as above. This time, the behavior of CH₄ was observed. Figure 6 shows unconverted CH₄ leaving the reactor increasing by increasing the time interval at 600°C. This happens because the pre-adsorbed CO₂ seems to have a very short lifetime on the catalyst's surface. This result is in good agreement with that obtained through CO₂ adsorption experiments. As already mentioned, the CO₂ adsorption on an oxidized surface of this catalyst is weak and reversible.

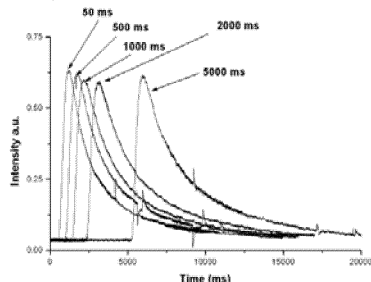


Fig. 5. CO₂ (probe molecule) responses at different time intervals and 600°C over 0.0125 g catalyst.

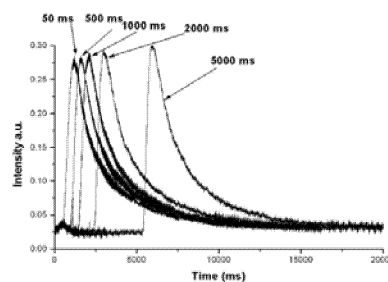


Fig. 6. CH₄ (probe molecule) responses at different time intervals and 600°C over 0.0125 g catalyst.

3.7. Hydrogen pulsing

The hydrogen behavior was checked during single-pulse TAP experiments with a H₂:Ar = 5:1 mixture, over an oxidized catalyst's surface. Figure 7 presents the H₂ responses against the Ar response, from RT to 600°C.

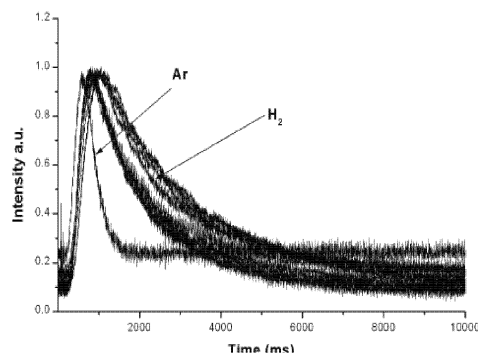


Fig. 7. H₂ response curves against Ar curve at increasing temperatures from RT to 600°C over 0.0125 g catalyst.

The H₂ responses narrow as the temperature increases. As a quite significant narrowing occurs for temperatures higher than 450°C, a stronger and irreversible adsorption of H₂ over this catalyst is supported by these TAP experiments. Indeed, the catalyst surface can be reduced by sending H₂ at temperatures higher than 450°C and this reduced surface proved to have higher activity for the dry reforming reaction than the oxidized one, as revealed by using a conventional plug-flow catalytic reactor (results not discussed here).

4. Conclusions

TAP single-pulse and alternating pulse experiments over the 5 wt% Ni/mesoporous silica catalyst revealed significant information on the behavior of this catalyst against diffusion, adsorption/desorption and reaction of different species involved in the dry reforming of methane with carbon dioxide.

First of all the effect of the intrapellet diffusion or pores diffusion was assessed through Ar single-pulse experiments. As the characteristic time of diffusion on the bed scale was of the same order of magnitude as the characteristic time of diffusion on the pellet scale, an overall Knudsen diffusion coefficient was determined. CH₄ and H₂ seemed to have an irreversible adsorption with reaction on the surface, while CO₂ show only a weak and reversible adsorption. The lifetime of CH₄ surface species was about 2000 ms.

References

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