Enhancement of Power-to-Gas via Multicatalyst Reactors Tailoring Reaction Rate and Heat Exchange

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Abstract: The Sabatier reaction is a key element of the power-to-gas development. For this reason, even though the process is known for more than a century, the Sabatier reaction is currently the object of important research efforts towards the development of new catalysts for performance improvement. However, the industrial exploitation of the Sabatier reaction depends on the development of reactors that match the best catalyst with an appropriate heat management. For this reason, this paper develops a methodology for the contemporary optimization of the reactor concept and the catalysts. It is observed that the reactor can be divided into three sections with contrasting requirements. In the first section, the main requirement concerns the reach of the reaction activation conditions. Hence, an adequate match between catalyst and reactor is needed, for example with an appropriate pre-heater. Once the reaction is activated, a reaction hotspot is formed, so that the cooling becomes determining and the main requirement for the catalyst is the resistance to poisoning and sintering. In the last section of the reactor, the low temperature activity of the catalyst is determining, so that a high-performance catalyst is needed. This paper indicates a strategy for the rational design of this catalyst, based on mechanistic evidence.

Keywords: Catalyst design · CO$_2$ methanation · Heat transfer · Reactor optimization

1. Introduction

The Sabatier reaction (also called CO$_2$ methanation) has gained significant interest over the last few years, thanks to the hypothesis that renewable H$_2$ will be widely available at low cost in the future.[1] The process to synthesize synthetic methane from renewable electricity is often referred to as power-to-gas. The reaction follows the stoichiometry:

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

$$\Delta H^\circ_R = -165.1 \text{ kJ/mol}$$  \hspace{1cm} (1)

On the common catalysts used for the Sabatier reaction, also the reverse water gas shift (RWGS) reaction occurs:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

$$\Delta H^\circ_R = +41.2 \text{ kJ/mol}$$  \hspace{1cm} (2)

At the same time, the produced CO can react with H$_2$ in the CO methanation reaction (linear combination of the two previous reactions):

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$

$$\Delta H^\circ_R = -206.3 \text{ kJ/mol}$$  \hspace{1cm} (3)

The reaction takes place over several metal-based catalysts, including Ni,[2–4] Co[5–7] and Ru.[8–10] All the above-mentioned catalysts show high selectivity to methane, but only Ru is active at sufficiently low temperature to achieve almost complete CO$_2$ conversion. In fact, the Sabatier reaction is limited by thermodynamics, so that high conversion is possible only below 300 °C.[11] Additionally, the current regulations for product injection in the natural gas grid are stringent. For example, the maximum allowed H$_2$ content in the gas grid in Switzerland is 2 vol./vol.%. [12] This often requires the installation of post-treatment units (e.g. membranes) to achieve the required gas purity.[13]

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significant research activities focused on the development of new catalysts, which combine the low cost granted by non-noble metals (e.g. Ni) with high activity.[14] However, the management of the Sabatier reaction goes beyond the catalyst design, as the industrial scale reactors show important elements of non-ideality, such as the presence of temperature hotspots. These may cause the instauration of significant transport limitations.[15,16] Hence, the optimally performing Sabatier reactor should be the sum of several optimization aspects, combining reactor and catalyst design in an appropriate way.

In order to address these elements, this paper develops an appropriate methodology to match reaction kinetics and transport phenomena, with the goal of designing the most cost-effective Sabatier reactor. In this sense, several different considerations are needed. First, an appropriate kinetic model for a reference catalyst is required. For the Sabatier reaction, numerous kinetic models are available both for the Ni-based and for Ru-based catalyst. Several of these models were recently summarized by Hernandez Lalinde et al.[17] (Ni-based) and by Falbo et al.[18] (Ru-based). The kinetic model allows the determination of the optimal trajectory a fluid particle should follow in the reactor, in order to minimize the size and cost of the equipment. This optimization can be performed, for example, with the methodology developed by Peschel et al.[19] In this way it is possible to identify sections of the reactor that are characterized by different requirements, in terms of rate-determining mechanism. For the Sabatier reactor, it was determined that the course of the reaction is characterized by three separated zones with different heat transfer requirements.[20] Initially, it is necessary to deliver heat to the reactants, to assure the reaction activation.[21,22] Later, once the reaction is started, the reactor requires intense cooling, due to the exothermicity of the process.[23,24] At the end of the reactor, the temperature must be kept constant to match thermodynamics and kinetics.[20] The determination of these different sections of the reactors has an important influence on the catalyst design, as each is characterized by a different dominating reaction mechanism and a different selectivity to the various products. This paper shows how to adapt the properties of the catalyst (independently from the active material chosen) in agreement with the design choices to yield an optimal reactor in terms of both reaction engineering and catalysis.

2. Methodology

2.1 Catalyst Synthesis

0.5 wt/wt.% Ru/Al₂O₃ was purchased from Sigma Aldrich. The pristine Ni and Co powders were purchased from Goodfellow (London, England). The main properties of the materials can be found in previous publications.[6,25] The powders were examined for purity by means of X-ray photoelectron spectroscopy (XPS) and no impurities other than oxygen and carbon on the surface were detected. XRD powder analysis was conducted, confirming the XPS results, showing that there are no impurities in the pristine metal catalysts. The pristine materials are used as purchased. The Ni/Mn/TiO₂ catalyst is synthesized by wet impregnation. The titania support was an AEROXIDE TiO₂ P-25 (Evonik), characterized by high specific surface area (BET surface area 50 m²/g) and by the presence of both rutile and anatase crystal structures. Ni(NO₃)₂·6H₂O (99.9%) and Mn(CH₃COO)₂·4H₂O (99.9%) from Sigma-Aldrich were used as Ni and Mn precursors without further purification. In the synthesis procedure, Ni(NO₃)₂·6H₂O (0.297 g) and Mn(CH₃COO)₂·4H₂O (0–0.501 g) were dissolved in 6 mL deionized H₂O. An appropriate amount of TiO₂ (ca. 2 g) was slowly added to the aqueous solution under stirring at room temperature. The resulting suspension was heated to 80 °C after 3 h to remove excess H₂O. The obtained solid was finally dried overnight at 110 °C in a static air oven. The Co/CoO catalysts are synthesized in situ starting from CoO₂. This precursor is reduced in H₂ with various temperature/time profiles to produce several self-supported catalysts with controlled ratios of Co and CoO, Co₂O₃ (0 < x < 1). CoO₂ was obtained by calcination of Co(NO₃)₂·6H₂O (Sigma-Aldrich, 98%) at 300 °C for 12 h followed by a temperature ramp of 2 °C min⁻¹ to 400 °C and then continued calcination for 2 h at 400 °C. To quantify the fraction of metallic cobalt on the surface of the Co₂O₃ₙ catalysts, samples were transferred to the XPS through a glovebox to avoid surface oxidation by the air. The XPS was equipped with a dual anode X-ray source and a Phobios 100 (SPECS GmbH) hemispherical energy analyzer. The Mg Kα (1253.6 eV) source was used for this study. The survey and narrow scans were collected at 90 eV and 20 eV pass energy, respectively.

2.2 Experimental Setups

The pristine metal experiments described in this paper were carried out in a gas controlling and analysis system equipped with three mass flow controllers (MFC). The reaction products were analysed and quantified by a mass spectrometer (MS-Pfeiffer OmniStar 320), using the calibration procedure and partial pressure determination described in ref. [26]. The MFCs are of the Bronkhorst El Flow series. The flow range is 0.4–20 ml/min and the absolute measurement error in ml/min is 0.1% of the maximum set point (20 ml/min) plus 0.5% of the set point. The reactor is a stainless-steel tube with a diameter of 7 mm in the reaction zone. The reaction zone starts 75 mm after the gas inlet. The catalyst is inserted after a small layer of glass wool is added on top of the in-tube sintered steel filter (Swagelok SS-2F-K4-60). The depth of the catalyst bed is measured to calculate the space velocity. The catalyst is then topped by another layer of glass wool in order to keep the material in place towards the reactor outlet.

The mechanistic investigations for the Ni/Mn/TiO₂ catalyst were performed by Quick X-ray Absorption Fine Structure (QEXAFS) and by SSITKA. The oxidation state and structure of the Ni and Mn phases were studied during catalyst reduction using QEXAFS. Measurements were done at the Ni K-edge (8.3 keV) and the Mn K-edge (6.5 keV) in transmission mode on beamline B18 at Diamond Light Source (Didcot, United Kingdom). In a typical SSITKA measurement, 200 mg catalyst was loaded into the stainless-steel reactor tube after dilution with SiC. The sample was reduced by heating in 50 mL/min of 20 vol % H₂ in Ar at a rate of 5 °C/min to 450 °C followed by an isothermal dwell of 2 h. The reactor was subsequently cooled in the same gas flow to 200 °C, and the total pressure was increased to 2 bar. Further details can be found elsewhere.[27,28] The mechanistic investigations for the Ru/Al₂O₃ and for the Co/CoO catalysts were performed using a Bruker Tensor 27 spectrophotometer with a resolution of 2 cm⁻¹, equipped with the Fraying Mantis accessory and high-temperature reaction chamber (HVC) from Harrick Scientific for the diffuse reflectance infrared Fourier transformation spectrophotometry (DRIFTS). The chamber was connected to He (purity 99.999%), H₂ (purity 99.999%), and CO₂ (purity 99.998%) gas lines and a turbomolecular pump. The background pressure was 1 × 10⁻⁵ mbar. The spectrophotometer was continuously flushed with clean dry compressed air. The peak assignment was done with an autonomous bi-level evolutionary Gaussian fitting (BEGF) procedure.[29]

2.3 Reactor Modelling

The design of the Sabatier reactor is performed by solving the mass and heat balances in a 1D heterogeneous reactor model (Eqs (4)–(7)):
The cooling medium is a thermal oil with inlet temperature of 200 °C. The catalyst efficiency factor is calculated via the Thiele modulus:

\[
\phi = \frac{V_p}{S_p} \sqrt{\frac{(n+1)}{2} \cdot \left(\frac{k c^{(n-1)}}{D}\right)} \tag{8}
\]

\[
\eta = \frac{3}{\phi} (\coth (\phi) - 1) \tag{9}
\]

The heat transfer is calculated as:

\[
\frac{1}{u_A} = \frac{1}{k_i} + \frac{k_c}{l_{in} \left(\frac{2}{r_e}\right)} + \frac{1}{k_e} \tag{10}
\]

k is calculated considering a stagnant and a dynamic contribution:

\[
k = \kappa_0 + 0.024 \cdot \frac{iR_e}{d_p} \tag{11}
\]

The kinetic models used for the simulations are specified in the results and discussion section.

3. Results and Discussion

3.1 Catalyst Isothermal Performance

In order to fully understand the basic performance of Ni, Co and Fe in the Sabatier reaction, the reactivity of the pristine materials was tested by recording the CO\(_2\) conversion in the range 200–550 °C. The results are shown in Fig. 1. As a benchmark, the reactivity of the commercial Ru/Al\(_2\)O\(_3\) catalyst is reported. All the curves are characterized by two different zones. Initially, the reaction is limited by kinetics, with the conversion progressively increasing with temperature. When the conversion approaches the thermodynamic equilibrium curve, the measured conversion decreases with the temperature, due to the prevalence of the thermodynamic limitations. The temperature of approach of the thermodynamic equilibrium is determining for the maximum CO\(_2\) conversion which can be achieved over a certain material, with a lower onset temperature corresponding to a higher conversion. The onset temperature can be determined as the temperature where 15–20% CO\(_2\) conversion is reached. Therefore, it is observed that cobalt activates at 280 °C and shows a maximum conversion of 70%. The Co curve is similar to the Ru/Al\(_2\)O\(_3\) curve, with a temperature shift of ca. 30–40 °C, resulting in a ca. 10% lower CO\(_2\) conversion. Ni is significantly less active in the Sabatier reaction, with an onset temperature of 380 °C and a maximum CO\(_2\) conversion of 55%. As the maximum conversion is achieved at 530 °C, a significant amount of CO is co-produced. Fe shows a low activity in the Sabatier reaction, as confirmed by the high activation temperature (540 °C), which leads to a predominance of the RWGS reaction.

The calculation of methane yield vs. temperature for Ru, Co and Ni is shown in Fig. 2. The calculated methane yield vs. temperature profiles for Ru/Al\(_2\)O\(_3\), Co and Ni are shown in Fig. 2. For Ru/Al\(_2\)O\(_3\) and Ni the kinetic models by Falbo et al.\(^{[30]}\) and by Xu and Froment\(^{[31]}\) are used. These models are chosen because they describe well the experimental results of Fig. 1. For the Co-based catalyst, the kinetic model developed in ref. [25] was used.

The low-temperature activity of the catalyst determines the activation temperature of the reaction. For all the catalysts considered, the reactor is subject to parametric sensitivity. This means that a critical set of conditions exists, for which the heat production is sufficient to cause a sudden reactor runaway and the for-
mation of a significant temperature hotspot. This phenomenon in reference to the Sabatier reaction has been widely discussed in literature. As the conditions of the simulated reactors are identical for the three catalysts, the different parametric sensitivity is reflected in a different reaction activation temperature. The reaction activation temperature is ca. 220 °C for Ru, 260 °C for Co and 340 °C for Ni. This corresponds approximately to the temperature for 10% CO conversion in the isothermal tests reported in Fig. 1. As parametric sensitivity is a distinctive character for fixed-bed catalytic reactors operating the Sabatier reaction, it is hard to avoid the formation of a significant temperature hotspot. This results in important challenges related to the handling of high temperature, but also gives the opportunity to utilize the high-temperature waste heat for process integration. In this sense, sufficient heat is available from the reaction to preheat the gas to the reaction activation temperature, even in the least favorable case of the Ni-based catalyst. Hence, in the design of the first section of the reactor, reaction engineering considerations are predominant over the catalyst design, as even a non-specific Ni-based catalyst can be successfully employed to initiate the reaction in an appropriately designed reactor.

Once the reaction is activated, the temperature rises until the gas mixture approaches the thermodynamic limit. In this section of the reactor, the reaction rates decrease drastically, due to the proximity to equilibrium. Hence, the heat transfer becomes limiting. In fact, the methane yield can increase only if the temperature is reduced. As the temperature is high, all the studied catalysts provide a sufficiently high reaction rate, so that the cooling rate is determining. This is visible in Fig. 2, where all the lines are overlap (light red area). However, special attention should be posed in this section to the possible problems related to catalyst deactivation. In fact, the high temperature may foster sintering phenomena as well as the possible catalyst poisoning due to CO formation in the RWGS reaction. For these reasons, an appropriate reactor design is essential to guarantee a good utilization of the catalyst and to minimize the equipment size. Efficient cooling can be achieved by maximizing the heat exchange surface and/or by enhancing the heat transfer (e.g. by using a boiling coolant). The catalyst choice is less critical than the reactor design in this section, so that a cheap, transition metal-based catalyst can be used. In order to avoid deactivation phenomena, the use of a resistant catalyst, for example tested for methane steam reforming, may be recommended.

When cooling lowers the temperature below ca. 400 °C, the reaction kinetics become determining. This is due to the reduced heat production, linked to the low amount of CO and H2 remaining. Hence, in this section, the catalyst gains a fundamental role in achieving the target methane yield. The dimensions of the reactor are here determined by the catalyst activity and by the possibility of reaching the required yield. If a catalyst is not suitable to achieve the desired yield, further purification steps in the downstream processing are needed. For this reason, it is of general interest to synthesize appropriate catalysts that ensure the required productivity. Fig. 2 shows the final performance of the catalyst studied. Ru/Al2O3 is suitable to produce grid-compliant synthetic methane, because it is active at low temperature (i.e. below 220 °C). However, Ru is significantly expensive that an alternative catalyst would be highly desirable. Ni can reach a maximum CH4 yield of ca. 90%, so that a significant performance improvement is needed. Co can reach 95% CH4 yield, hence needing a limited optimization to reach the target result. Note that, in any case, the fraction of the reactor requiring a high-performance catalyst is limited.

### 3.3 Catalyst Design

In order to rationally design an effective catalyst, the mechanistic understanding of the reasons that make Ru highly active is necessary. To this end, a detailed *operando* analysis of the reaction intermediates in the Sabatier reaction over 0.5 wt.% Ru/Al2O3 catalyst was performed by means of DRIFTS. It was observed that carbon monoxide (CO) adsorbed on the metallic surface is the key intermediate for methane production. This species is formed by decomposition of the adsorbed bicarbonate (HCO3−), which in turn directly originates from the adsorption of CO2 from the gas phase. Bicarbonate is formed at low temperature on the metal-support interface. Hence, the specific configuration of this specific adsorption site is essential for the low temperature activity of the catalyst. The reaction mechanism is schematized in Fig. 3: CO2 is adsorbed on the support in various forms, according to the process conditions. The first key intermediate, HCO3−, is formed at the metal-support interface. This species decomposes, in the presence of H2, to produce the second key intermediate, CO, on the metallic surface. The optimal low-temperature performing catalyst should then provide the right combination of the different sites to maximize the reaction rate for these steps.

![Fig. 3. The predicted general reaction mechanism: the active sites operate as H2 adsorption location, while the support is the main adsorption site for CO2, operating as carbon sink. The rate-determining step occurs at the interface between metal and support.](image)

On the basis of this information, initially Co was targeted as active phase for the optimized catalyst. In order to produce sufficient interfaces between the metal and the support (CoO) the catalyst was synthesized *in situ* by reduction of CoO. The influence of the metallic Co fraction on the 20% CO2 conversion temperature is shown in Fig. 4. The plot shows a clear minimum at 20% metallic Co fraction. This means that the low temperature activity of the Co-based catalyst can be significantly increased by tailoring the relative amount of metallic and oxidized sites. The analysis of the surface species by DRIFTS revealed that the enhanced activity of the sample with 20% metallic Co is due to a higher activity in the CO2 adsorption and in the formation of oxygenated adsorbed species at the metal/support interface. Hence, the control of the availability of the interface and the presence of an oxide support phase operating under these conditions is crucial for the synthesis of grid-compliant methane.
as reservoir for the adsorbed species is the key for the synthesis of a low-temperature active catalyst for the CO₂ methanation.

The reactor is divided in three sections. In the first section, a simple Ni catalyst can be used, provided that the reaction activation is ensured by a careful preheating. This is done, for example, by recovering the heat from the product stream prior to water condensation or by using the waste heat from the reaction.

In the second zone, the heat transfer must be maximized, and the catalyst should be resistant to the high temperature of the reactor hotspot. This can be achieved, for example, by using a Ni/MgAl₂O₄ catalyst (from methane steam reforming) and a series of pipes with small diameter. In the last section, a tailored-made catalyst for the Sabatier reaction is required, to achieve high conversion. In this part of the reactor the only requirement for the reactor design is the preparation of isothermal conditions. The catalyst should instead be carefully designed to enhance the rate-determining step of the reaction, allowing the operation at low temperature. This last section can be operated both on Co or Ni, according to the specific requirements of the system to design. Note that the design of the previous sections is essential for the good functioning of this part of the reactor, because the eventual CO formed in the reaction hotspot should be converted prior to the inlet of this last zone. In fact, only by eliminating all the residual CO₃ is it possible to avoid deactivation phenomena due to blocking of the active sites on the metal/support interface.[28]

4. Conclusions

This paper showed how the interplay of reactor and catalyst design is essential to design an optimal process for the CO₂ methanation. Primarily, reaction engineering considerations are required to define the determining element among kinetics, thermodynamics, heat and mass transfer in the various section in which the reactor can be divided. These reflections already provide the indication of the optimal catalyst to employ, which, for some sections, may not correspond to the optimal catalyst for the target reaction. In fact, under certain conditions, side reactions may become dominating, hence the presence of additional components must be considered. When the reaction kinetics are not determining, the main focus should involve the design of an appropriate reactor configuration to minimize the effect of the other limiting factors. When, however, the reaction kinetics are determining, the optimal reactor directly depends on the maximization of the catalyst performance. It was shown that the rational design of an optimal catalyst should follow the determination of the essential characteristics that enhance the reaction rate. For the Sabatier reaction, the crucial element to establish is the correct ratio of oxidized and reduced sites, to ensure the formation of the CO₂ adsorption species and their fast conversion towards methane. It was shown that this is possible either by synthesizing in situ a catalyst with an appropriate formulation (in the Co case) or by adding a suitable promoter, adjusting the metal oxidation temperature (in the Ni case). The result of this unified reactor and catalyst design is an optimized reactor that combines all the required elements to maximize the productivity.
This methodology, here applied to the Sabatier reaction, may be, in principle, extended to any catalytic reaction.

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