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Kinetics of the hydrogenation of CO_2 to methanol at atmospheric pressure using a Pd-Cu-Zn/SiC catalyst

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ABSTRACT

The kinetics of the hydrogenation of CO_2 to methanol (MeOH) at atmospheric pressure using a Pd-Cu-Zn/SiC catalyst has been analyzed. An initial sensitivity study was performed in order to evaluate the effect of reaction conditions (temperature, CO_2/H_2 ratio and the presence of products in the feed stream) on the catalytic performance. The results of this study were used to develop three Langmuir–Hinshelwood kinetic models in which the adsorption term was modified (competitive vs two-site vs three-site adsorption mechanism). All of the kinetic models predicted the experimental results well and the corresponding parameters were statistically meaningful. Model discrimination revealed that the three-site adsorption mechanism led to the lowest residual sum of squares and was the only one that met all of the parameter constraints. The quality of this model was evaluated by comparing the results of additional experiments with the predicted values. The three-site adsorption mechanism agreed with the catalytic observations reported previously, where it was observed that, in the presence of a Pd-Cu-Zn/SiC catalyst, the synthesis of MeOH by hydrogenation of CO_2 took place on PdZn active sites, whereas the Reverse Water Gas Shift (RWGS), which led to CO, was catalyzed by PdCu sites. The H_2 dissociative adsorption was believed to take place on ZnO.

1. Introduction

Carbon dioxide is considered to be the main contributor to global warming and it is therefore one of the most harmful pollutants to the ecosystem [1]. At the same time, it is one of the most promising sources of carbon to produce other compounds such as hydrocarbons, alcohols, and aldehydes, among others [2]. In this regard, the scientific community is working on the development of processes to transform the CO_2 pollution problem into an opportunity to obtain valuable products.

The hydrogenation of carbon dioxide to methanol (MeOH, Eq. (1)) is one of the ways in which this pollutant can be valorized [3]. MeOH is frequently used as a solvent and a feedstock to produce chemicals. MeOH could be used as a fuel in the energy distribution infrastructure that currently exists, in a direct MeOH fuel cell [4], or it could be blended with gasoline [5].

$$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O \quad \Delta H_{25°C} = -49.5 \text{ kJ·mol}^{-1} \quad (1)$$
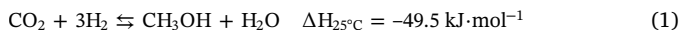
The reverse water gas shift reaction (RWGS, Eq. (2)), which also participates in the hydrogenation process, leads to carbon monoxide and this is considered to be an undesirable by-product. In this sense, the use of catalysts in order to improve the MeOH selectivity and the CO_2 conversion is crucial.

$$CO_2 + H_2 \leftrightarrows CO + H_2O \quad \Delta H_{25°C} = 41 \text{ kJ·mol}^{-1} \quad (2)$$
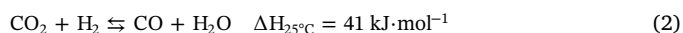
Up to date, the vast majority of the research concerning this reaction is focused on the development of novel catalysts. In this regard, Wisaijorn et al. [6] modified copper-based catalysts by oyster shell-derived calcium oxide, and concluded that this material can prevent sintering of Cu particles and promoted the adsorption of CO_2. Zhao et al. [7] used Atomic Layer Deposition (ALD) to deposit Ni particles over Cu/Al_2O_3 catalysts, which led to the formation of CuNi alloys which were active in this reaction. Another example is the work reported by An et al. [8], who supported in situ Cu/ZnO_x nanoparticles in Metal-Organic Frameworks (MOFs), at a reaction temperature of 250 °C under hydrogen atmosphere. As a result, they obtained ultra-small Cu/ZnOx nanoparticles which showed high catalytic activity and selectivity to methanol.

Several different kinetic models for the synthesis of MeOH by CO_2 hydrogenation have been reported in the literature to date. Skrzypek et al. [10] proposed a Langmuir–Hinshelwood (LH) kinetic model that considers the competitive adsorption of species. Graaf et al. [11] supposed a dual-site mechanism in which H_2 and H_2O are adsorbed by ZnO

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Nomenclature

C_S	CO_2 surface concentration
D_{eff}	Catalyst effective diffusivity [m²/s]
D_x	Adsorption terms
Ea_x	Activation energy [kJ/mol]
F_{Pi}	Species molar flow
ΔH	Heat of reaction [kJ/mol]
ΔH^0_{ads}	Enthalpy of adsorption [kJ/mol]
k'_x	Reaction rate constant
$K_{i,S}$	dsorption equilibrium constant of species i in the active site s
Keq_x	Equilibrium constant of reaction rate
n	Number of data
N_{W-P}	Weisz–Prater number
p	Number of parameters
P_i	Partial pressure of the component i [bar]
R	Gas constant [R = 8.314 J/mol·K]
r	CO_2 initial conversion rate [%]
r_x	Reaction rate [mol_i/g_{cat}·min]
r^2	Regression coefficient

s_1	PdZn active site
s_2	ZnO active site
s_3	PdCu active site
s_i	Residual ($P_{iexp} - P_{itheo}$)
ΔS^0_{ads}	Entropy of adsorption [kJ/mol·K]
T	Temperature [K]
W	Catalyst mass [g]
w	Weighting factor
WRSS	Weighted Residual Sum of Squares

Greek Letters

ρ_c	Catalyst density [kg/m³]

Subscripts

exp	Experimental data
i	Species
theo	Theoretical data
x	Reactions (MeOH-CO_2, RWGS, MeOH-CO)

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active sites and carbonaceous species by metallic copper sites. This model has also been proposed by several authors [13]. Finally, Park et al. [12] supposed a three-site adsorption mechanism, where the adsorption of hydrogen occurs on ZnO whereas CO and CO_2 are adsorbed on Cu^{1+} and Cu^0, respectively. The vast majority of the kinetic models, such as those outlined above, have been developed using commercial $Cu/ZnO/Al_2O_3$ catalysts and only some few ones have been developed with other catalyst configurations, such as $Cu/ZnO/Al_2O_3/ZrO_2$ [13] or Pd-Ga_2O_3/Silica [14]. Moreover, only Chiavassa et al. [14] studied exclusively the hydrogenation of CO_2.

In our previous work [15], we optimized a PdCuZn/SiC catalyst by modifying the Pd/Cu ratio. Taking into account the secondary role of Zn in this reaction (hydrogen adsorption and dissociation), a highly enough proportion of this metal was deposited in each catalyst. On the other hand, as Pd and Cu are reported to be active phases in this reaction, the proportion of these metals was modified in a broad range in order to get an optimal trimetallic formulation, which was more active and selective than the corresponding bimetallic ones. By doing this, it was possible to tailor the formation of PdZn and PdCu nanoparticles which catalyzed the synthesis of methanol (Eq. (1)) and inhibited the RWGS (Eq. (2)), respectively, thus obtaining an optimum trimetallic formulation (see below) that maximizes the methanol formation rate. This catalyst formulation will be used in the later stage of the project, in which an electrocatalytic reactor, operating at atmospheric pressure, will be developed for the synthesis of methanol with a feed of CO_2 and H_2O. This electrocatalytic reactor will have two chambers separated by a co-ionic ceramic conductor. Water splitting will take place in the anodic chamber, whereas methanol synthesis will occurred in the cathodic one. By application of an electrical current, the system will act as an electrochemical hydrogen/oxygen pump (H^+ will be pumped to the cathode and O^{2-} will be pumped away from the cathode). Under this mode of operation, controlled H^+ fluxes to the cathodic catalyst are expected to create high surface hydrogen activities, which in turn will force equilibrium to the production of methanol, bypassing the conventional necessity for high pressure. At the same time O^{2-} pumping from the cathode is expected to activate the C=O bond of the adsorbed CO_X species, so that methanol synthesis will be accelerated. This way, it is expected to overcome the two main drawbacks of the so-called conventional catalytic operation: the need of high pressure operation and fossil fuel-derived hydrogen gas.

The aim of the work described here was to perform the kinetic analysis and modeling for the synthesis of MeOH by CO_2 hydrogenation

at atmospheric pressure, using the PdCuZn/SiC catalyst above mentioned, as a prior step to the development of the electrocatalytic reactor. Firstly, a sensitivity study was carried out by varying the composition of the feed stream and the temperature. Secondly, three different Langmuir-Hinshelwood kinetic models were developed as a function of the adsorption mechanism. Finally, the proposed models were compared and a proper model discrimination was carried out.

2. Experimental

2.1. Catalyst preparation and characterization

A PdCuZn/SiC catalyst with a molar percentage of 37.5% Pd, 12.5% Cu and 50% Zn (0.01 total moles) was used in this work. All of the information related to the preparation and characterization (N_2 Adsorption/Desorption, XRD, TPR, TEM, XPS) was published in a previous paper by our group [15]. This tri-metallic catalyst showed better catalytic performance in the hydrogenation of CO_2 to MeOH than the bi-metallic PdZn/SiC and CuZn/SiC counterparts.

2.2. Catalyst activity measurements

Catalytic tests were carried out in a tubular quartz reactor (45 cm length and 1 cm diameter). The catalyst, which consisted of pellets that were 3 mm in length and 1 mm in diameter, was placed on a fritted quartz plate located at the end of the reactor. The amount of catalyst used in the experiments was 0.8 g.

The temperature of the catalyst was measured with a K-type thermocouple (Thermocoax) placed inside the inner quartz tube. The entire reactor was placed in a furnace (Lenton) equipped with a temperature-programed system. Reaction gases were Praxair certified standards of CO_2 (99.999% purity), H_2 (99.999% purity), N_2 (99.999% purity), CH_3OH (0.5% diluted in N_2) and CO (99.999% purity). The gas flows were controlled by a set of calibrated mass flowmeters (Brooks 5850 E and 5850 S).

The hydrogenation of CO_2 was carried out at atmospheric pressure. The feed composition was different in each experiment, keeping the total flow at 110 Nml·min⁻¹, using N_2 as a balance (GHSV = 6600 h⁻¹). The specific compositions used in all experiments are listed in Table 1. Experiments with CO_2 and H_2 in the feed stream were carried out at 473, 498, 523 and 548 K. The rest of the experiments, in which CO or MeOH were added to the feed, were evaluated at