Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Methanation of carbon dioxide on Ru/Al_2O_3: Catalytic activity and infrared study

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ARTICLE INFO

Article history:
Received 3 August 2015
Received in revised form 29 October 2015
Accepted 18 December 2015
Available online xxx

Keywords:
Methanation
CO_2
Ruthenium on alumina
Hydrogenation
Methane
Surface species

ABSTRACT

3% Ru/Al_2O_3 catalyst is active in converting CO_2 into methane at atmospheric pressure. At 673 K and above the thermodynamic equilibrium is nearly attained. At 623 K CH_4 yield is above 85%. CO selectivity increases by decreasing reactants partial pressure apparently more than expected by thermodynamics. The reaction order for CO_2 partial pressure is confirmed to be zero, while that related to hydrogen pressure is near 0.38 and activation energy ranges 60–75 kJ/mol. Arrhenius plot demonstrates that only at reduced reactant partial pressure (3% CO_2) or high contact times, a contribution due to some diffusional limitation is present. IR study shows that the H_2—reduced catalyst has high-oxidation state Ru oxide species able to oxidize CO to CO_2 at 173–243 K, while after oxidation/reduction cycle the alumina surface acido-basic sites are freed and the catalyst surface contains both extended Ru metal particles and dispersed low valence Ru species. IR studies show that the formation of methane, both from CO and CO_2, occurs when both surface carbonyl species and surface formate species are observed. Starting from CO_2, methane is formed already in the low temperature range, i.e., 523–573 K, even when CO is not observed in the gas phase.

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1. Introduction

The conversion of CO_2 into methane (methanation)

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (1)$$

is one of the possible ways to utilize carbon dioxide thus reducing emissions [1], when hydrogen produced by renewable raw materials or using waste energy is available [2]. To date, commercial catalysts optimized for methanation of feeds primarily composed of carbon dioxide are apparently lacking. Conventional methanation catalysts, optimized to convert feeds containing primarily carbon monoxide, have been mostly tested as CO_2 methanation catalysts and generally found active [3]. Although commercial Ni-based CO methanation catalysts have been found to be active also for CO_2 methanation [4,5] they usually also coproduce significant amounts of CO. Ru based catalysts have been reported since decades to be among the best catalysts for CO_2 methanation [6]. Although Ru/TiO_2 [7], Ru/SiO_2 and Ru/ZSM5 zeolite [8] have also been reported to be very active, a number of studies show good performances of Ru/Al_2O_3 catalysts [9–11], essentially better than Ni/Al_2O_3 catalysts [12]. On the other hand, Ru/Al_2O_3 catalysts are commercial catalysts for CO methanation for low temperature applications ($T < 443$ K), such as the Clariant METH-150 catalyst that contains 0.3% ruthenium on alumina [13]. Interestingly, supported ruthenium catalysts are also reported to be the best for CO hydrogenation to higher hydrocarbons, i.e., the Fischer Tropsch process [14,15]. Obviously, for the development of a performant CO_2 methanation process, catalysts producing methane with high selectivity, thus with low CO and higher hydrocarbons coproduction, must be developed.

A point closely related to reaction selectivity is that of reaction mechanism. Until the 1970s, the mechanism of CO methanation was supposed to occur through oxygenated intermediates [6], supported also by more recent spectroscopic studies [16]. However, most recent studies tend to prefer a "via carbide" mechanism, mainly based on "surface science" investigations performed on metal monocrystals. As for the mechanism of CO_2 methanation, an

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http://dx.doi.org/10.1016/j.cattod.2015.12.010
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Please cite this article in press as: G. Garbarino, et al., Methanation of carbon dioxide on Ru/Al_2O_3: Catalytic activity and infrared study, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2015.12.010

additional central point concerns the possible role of CO, produced by the reverse Water Gas Shift reaction (rWGS)

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (2)$$

as an intermediate, or/and as a competitor [17,18], the possible intermediacy of carbide species as well as the possible role of the support in adsorbing and activating CO_2 [19].

To have more information on the surface chemistry of an active Ru/Al_2O_3 catalyst and on mechanistic aspects, we deepened our previous studies with further flow reactor experiments and by applying IR spectroscopy methods.

2. Experimental

2.1. Catalyst characterization

The catalyst used in this study is a 3% (wt%) $Ru/\gamma\text{-}Al_2O_3$ commercial catalyst (S_{BET} 150 m^2/g) from Acta S.p.A. (Crespina, Pisa, Italy).

IR spectroscopy experiments were performed using a Nicolet Nexus FT instrument. Pressed disks of the pure catalysts powders were treated "in situ" by using an infrared cell connected to a conventional gas manipulation/outgassing ramp in two different ways: by a simply reduction in H_2 (500 torr) at 673 K for 1 h followed by vacuum treatment at 773 K for 30 min. Alternatively, an oxidation step in air (200 torr) at 673 K for 30 min followed by the same reduction procedure was conducted. The catalyst disk was first submitted to activation and then CO adsorption and reaction experiments were carried out.

CO adsorption was performed at 140 K by the introduction of a known dose of the gas (10 torr) inside the low temperature infrared cell containing the previously activated wafers. IR spectra were recorded during evacuation upon warming at increasing temperatures between 140 K and 673 K.

For the reaction experiments a mixture of H_2 and CO_2 (17 torr CO_2 and 170 torr on IR line and cell) and one of H_2 and CO (17 torr CO and 170 torr on IR line and cell) were put in contact with the catalyst disk and the reaction was performed step-by-step in-between 523–773 K for ten minutes at each temperature; for each reaction temperature IR spectra of both the gas phase and the catalyst surfaces were acquired.

2.2. Catalytic experiments

Catalytic experiments were carried out in a fixed-bed tubular silica glass flow reactor, operating isothermally, loaded with 700 mg of silica glass particles (60–70 mesh sieved) as an inert material mixed with variable amounts of catalyst powder. Different gaseous mixtures of CO_2 and H_2 (with excess H_2) diluted with nitrogen were fed, with a total gas flow of 75 ml_{NTP}/min. Temperature was varied step by step in-between 523 K and 773 K (ascending temperature experiment) and back down to 523 K (descending temperature experiment). GHSV calculated as volumetric flow rate (NTP), v [ml/h] versus catalyst volume V_{cat} [ml] was varied in between 15000 and 55000 h^{-1}. These values correspond to 5300 and 8000 h^{-1} if space velocity is calculated taking into account the entire bed volume V_{tot}, constituted by silica glass and catalyst powder. Hereinafter we will always refer to the GHSV calculated on the catalyst volume.

Products analysis was performed on line using a Nicolet 6700 FT-IR instrument. Frequencies where CO_2, CH_4 and CO molecules absorb weakly have been used (2293 cm^{-1} for CO_2, 2100 cm^{-1} for CO, 1333 cm^{-1} for CH_4, after subtraction of baseline water absorption) with previous calibration using gas mixtures with known concentrations, in order to have quantitative results. Produced water was mostly condensed before the IR cell. From the inlet and outlet concentrations calculated from the absorbances of CO, CO_2, CH_4 and the measured inlet and outlet total flows (which allow to take into account the variation of the number of moles during the reaction), CO_2 conversion (X_{CO_2}), selectivities and yields to products, S_i and Y_i, have been calculated [20]. They are defined as:

$$X_{CO_2} = \frac{F_{CO_2 in} - F_{CO_2 out}}{F_{CO_2 in}} \quad (3);$$

$$S_i = \frac{F_i}{F_{CO_2 in} - F_{CO_2 out}} \quad (4);$$

$$Y_i = \frac{F_i}{F_{CO_2 in}} \quad (5);$$

where F_i is the molar flow rate of i (i.e., CO and CH_4), while F_{CO2} is the molar flow rate of CO_2 and they were all expressed in mol/min.

From the kinetic orders determined in our previous study and from the production rate of CH_4 we calculated the kinetic constant k [mol/(min × g_{cat} × $atm^{0.38}$)] designing for each test the Arrhenius plot in order to have a better understanding of the controlling regime in the different conditions [12,21].

It should be remarked that, as already reported in our previous work [12], we did not observe any coke formation in our experiments performed at the 8 h timescale. Carbon balance is 100% ± 1% to our calculations and no evidence of coke was obtained from the catalyst weight measure nor from IR, UV–vis, FE-SEM and XRD studies.

3. Results and discussion

3.1. CO_2 methanation in flow reactor

In Fig. 1, the results of flow reactor CO_2 methanation experiments (line + symbols) on the 3% Ru/Al_2O_3 catalyst are reported and compared with the respective thermodynamic equilibrium for each condition. The three experiments have been performed with the same H_2/CO_2 ratio of 5 at 1 atm and the same space velocity (55,000 h^{-1}), but with different reactant concentrations. In all cases, no other products than methane and CO were detected. The C balance was always fully fulfilled and no evidence of carbon formation was found using IR, UV–vis, FE-SEM and XRD techniques.

The fresh catalyst is almost not active at 523 K and is only poorly active at 573 K (3% CO_2 conversion), with a small methane yield slightly increasing with time on stream. In the step performed at 623 K, the catalyst starts to have significant activity that definitely increases with time on stream, due to an activation or "conditioning" step. According to our previous study [12], the catalyst is activated essentially by reduction from a partially cationic to a metallic state. In these conditions, selectivity to methane is 100%, except for the most diluted conditions, where CO is coproduced in small amounts (2–5% yield). At 673 K, CO_2 conversion is high (from 80% to 84% and from 72% to 79% for 9% CO_2 and 6% CO_2 cases, respectively) but still growing with time on stream (Table S1), showing that a "conditioning" effect was still in progress, except again for the most diluted conditions, where the catalyst appears already stable, achieving a CO_2 conversion of 60% with a methane yield of 47%. At this temperature, CO was also formed together with methane, in particular in the most diluted conditions with a yield of 14%. On the other hand, at the end of the experiments at 673 K the conversion of CO_2, the methane yield and selectivity depend clearly on concentration of the reactants, being larger (83–84% for CO_2 conversion and 82–83% methane yield) when the reactants were more concentrated. By comparison with calculated thermodynamic equilibrium data (Fig. 1 and Table S2 calculated according to [22]), CO_2 conversion is still markedly lower than the equilibrium one. Thus, the reaction is still under kinetic control, maybe

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