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Short communication

Effect of syngas conversion and catalyst reduction temperature in the synthesis of ethanol: concentration of water vapor in mesoporous Rh/MCM-41 catalyst

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ABSTRACT

Rh-based catalysts typically show low selectivity to CO_2 in the synthesis of ethanol from syngas. However, a novel mesoporous Rh/MCM-41 catalyst shows high selectivity to CO_2 in a large range of syngas conversions; 1% to 68%, regulated by adjusting the operation conditions (270–430 °C, 30–90 bar and 6000–40,000 $ml_{(syngas)}/g_{cat}$ h). The same effect is obtained at different catalyst reduction temperatures (200 °C and 500 °C) as well as on the non-reduced catalyst. A high concentration of water vapor seems to occur in the pores of Rh/MCM-41 which may promote the water-gas-shift-reaction, producing extra CO_2 and H_2.

1. Introduction

Over the past decade, ethanol-grade fuel has been widely used in the transportation sector as a renewable fuel component, blended with gasoline or as pure fuel in flex-fuel vehicles [1,2]. Most of the ethanol-grade fuel is produced via biochemical processing of food-related resources, such as corn grain in the USA or sugar cane in Brazil. Some controversial issues arise about the long-term sustainability of these resources, in addition to economic challenges as well as policy uncertainty [1]. The development of alternative processes using nonfood-related resources like cellulosic biomass (wood, waste wood, municipal solid waste or others) is under R&D stages by academic, private and government institutions in different places around the world [3].

Cellulosic biomass can be converted into fuels and chemicals thermochemically [4]. In the thermochemical process, the biomass feedstock is first converted to an intermediate mixture of gases known as "synthesis gas" or "syngas". Then the generated syngas is catalytically converted to the final product. The rhodium-based catalysts are among the most selective catalysts reported to convert syngas into ethanol [5, 6]. However, few reports are found using mesoporous silica as catalyst support [7–10], although various mesoporous materials have been applied in other catalytic systems showing interesting results [11–13]. Mesoporous silica MCM-41 has 1D-hexagonal porous arrangement with a pore diameter of 1.6–10 nm and a wall thickness of around 0.8 nm [14,15]. MCM-41 has a large surface area, usually 1000 m^2/g or more, which can be of great utility for dispersing the active sites and thus boost the catalyst activity per unit of mass.

Typically a low selectivity to CO_2 is reported for the Rh-based catalysts [6]. However, during a preliminary catalytic testing of a novel mesoporous Rh/MCM-41 catalyst, a high selectivity to CO_2 was observed at low syngas conversion (<3%). This might suggest a concentration of water vapor in the catalyst porous, which could promote the water-gas-shift-reaction (WGSR). The occurrence of the WGSR in Rh/MCM-41, at the same time, could change the product selectivity as compared to typical Rh/SiO_2. Therefore, it become interesting to evaluate the catalytic performance of a mesoporous Rh/MCM-41 catalyst at different levels of syngas conversion and their effect over the CO_2 formation (extent of the WGSR) as well as the overall product selectivity.

In the present work, we have varied the syngas conversion from 1% to 68% by changing the operation conditions; 270–430 °C, 30–90 bar and 6000–40,000 $ml_{(syngas)}/g_{cat}$ h. The effect on CO_2 formation and product selectivity is presented for the mesoporous Rh/MCM-41 and compared to the results obtained using a typical Rh/SiO_2 catalyst. In addition, the effect of the catalyst reduction temperature (200 °C and 500 °C) has been evaluated and compared with the non-reduced catalysts. These results and a more detailed discussion will be published elsewhere.

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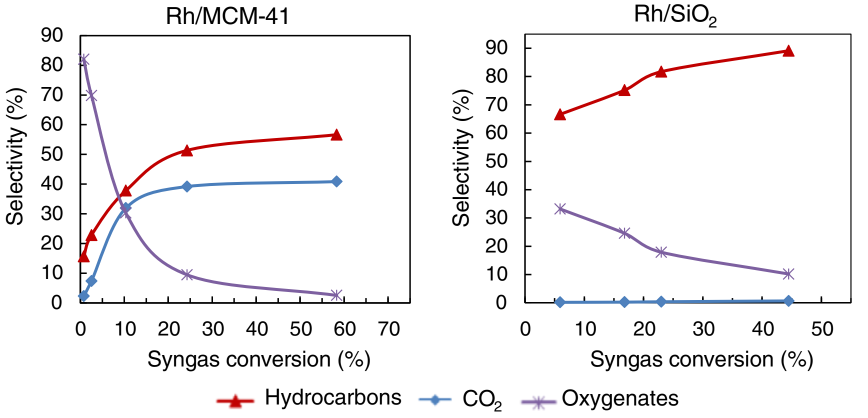

Fig. 1. Effect of syngas conversion on the product selectivity over Rh/MCM-41 and Rh/SiO_2 catalysts. Catalysts pre-reduced at 200 °C. Hydrocarbons: C_1–C_5 linear alkanes, oxygenates: C_1–C_4 linear alcohols, acetaldehyde, acetic acid and esters.

2. Experimental

2.1. Catalyst preparation and characterization

Mesoporous silica (MCM-41) was prepared by "the atrane route" [17]. The method is based on the use of a cationic surfactant (cetyltrimethylammonium bromide), as the structural directing agent, and a complexing polyalcohol (2,2′,2″-nitriletriethanol or triethanolamine) as a hydrolysis retarding agent. The synthetic procedure is described elsewhere [17,18]. A commercial MCM-41 was purchased from Sigma Aldrich which was indistinctly used to the MCM-41 prepared from "the atrane route". Silica (SiO_2) catalyst support was purchased from Alfa Aesar. The Rh/MCM-41 and Rh/SiO_2 catalysts were prepared by successive incipient wetness impregnation of MCM-41 and SiO_2, respectively, using an aqueous solution of $RhCl_3 \cdot nH_2O$. After impregnation, the catalysts were dried at 120 °C for 1 h and then calcined at 500 °C for 5 h. The metal loading was 3 wt.% Rh for both catalysts. Detailed catalyst characterization will be published elsewhere, including H_2-TPR, XPS, N_2-physisorption, XRD, H_2-chemisorption and TEM analyses.

2.2. Catalytic testing

A down-flow fixed bed reactor was used for the catalytic testing. The internal diameter of the tube reactor is 8.3 mm, where 200–600 mg of catalyst was charged. The catalyst particle size was between 106 μm and 250 μm. The reactor components and the on-line gas chromatograph (GC) analysis have been previously described by our group [19]. N_2 was used as internal standard to quantify CH_4, CO and CO_2 using a thermal conductivity detector. The internal normalization of corrected peak areas was applied to quantify hydrocarbon and oxygenated compounds in a flame ionization detector [20]. The expressions for calculating the syngas conversion level, product selectivity (in terms of carbon mol) and carbon balance are described in [19]. Premixed syngas (AGA Linde) with a H_2/CO ratio of 2:1 was used for all the experiments.

In order to evaluate the effect of the catalyst reduction temperature, the catalysts were reduced prior to the reaction with pure H_2 (50 ml/min) at two different temperatures: 270 °C and 500 °C. For comparative purposes the non-reduced catalysts were also evaluated. After reduction, the catalyst was cooled to reaction temperature in He, then the system was pressurized to reaction pressure with syngas. The reaction conditions (temperature, pressure and gas-hourly-space-velocity) were varied in order to obtain a syngas conversion between 1% to 68%; 270–430 °C, 30–90 bar and 6000–40,000 $ml_{(syngas)}/g_{cat}$ h. At each reaction condition, a pseudo-stationary state was achieved after 15–20 h under syngas stream. The carbon balance in all the experiments was between 99.0% and 100%.

3. Results and discussion

3.1. Effect of syngas conversion

The effect of syngas conversion on the product selectivity obtained for the Rh/MCM-41 and Rh/SiO_2 catalysts is shown in Fig. 1. The catalysts were reduced before reaction at 200 °C. The products are hydrocarbons (C_1–C_5 linear alkanes), oxygenates (C_1–C_4 lineal alcohols, acetaldehyde, acetic acid, methyl acetate and ethyl acetate) and CO_2. For both catalysts, it can be observed that by increasing the syngas conversion the selectivity to hydrocarbons is increased, while, in contrast, the selectivity to oxygenates is decreased. In particular, the selectivity to oxygenates is notably increased at very low syngas conversion in the Rh/MCM-41 catalyst. It can also be seen that while almost no CO_2 is formed over the typical Rh/SiO_2 catalyst, a high CO_2 selectivity is observed over the mesoporous Rh/MCM-41 catalyst, in the whole range of syngas conversion studied.

At same reaction conditions, the mesoporous Rh/MCM-41 catalyst also shows higher selectivity to CO_2 than the Rh/SiO_2 catalyst, as can be observed in Table 1. This indicates a preferential formation of CO_2 over the mesoporous Rh/CM-41 catalyst that may be due to a concentration of water vapor in the catalyst pores. In a separate experiment, water vapor was added to the syngas feed-stream, which resulted in an even more CO_2 selectivity; 90% CO_2 with addition of water vapor and 4.1% without addition of water vapor (280 °C, 20 bar, 3000 ml/g_{cat} h). The latter result supports that some water vapor can be concentrated in the pores of Rh/MCM-41, which may promote the WGSR producing extra CO_2 and H_2. It seems that no concentration of

Table 1
Catalytic performances of Rh/MCM-41 and Rh/SiO_2 catalysts.

Catalyst	BET area (m^2/g)	Pore diam. (nm)	T (°C)	P (bar)	GHSV (ml/g h)	Conv. (%)	HC (%)	CO_2 (%)	Oxy. (%)
Rh/MCM-41	961	3.4	280	20	12,000	2.8	48	4.1	47.9
			300–400	30–90	3200–20,000	0.8–58	16–57	2–41	3–82
Rh/SiO_2	236	12	280	20	12,000	2.8	58	0.3	41.7
			270–350	90	13,000	6–45	67–89	0.2–0.7	10–33