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ScienceDirect

Catalysis Today 133–135 (2008) 136–141

CATALYSIS TODAY

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Characterization of ZnO and TiO_2 catalysts to hydrogen production using thermoprogrammed desorption of methanol

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Available online 8 February 2008

Abstract

Mixed zinc, titanium and alumina oxides were characterized by X-ray diffraction (XRD) and TPD-methanol techniques. The surface properties were correlated with the products from methanol decomposition. XRD results showed that 20% of ZnO supported on Al_2O_3 and on TiO_2/Al_2O_3 formed zinc aluminate phase. However, 20%ZnO/TiO_2 and 20%TiO_2/Al_2O_3 presented the characteristic structure of the oxides as segregated phases. TPD-methanol results for 20%TiO_2/Al_2O_3 sample showed an intense CO desorption, which was associated with a large density of Lewis acid sites due to TiO_2 surface and to the Lewis and Brönsted acid sites of alumina. On the other samples, the higher density of basic sites and weak Lewis acid site was related to ZnO presence that increased the CO_2 desorption. The high H_2/CO_2 ratio and the absence of CO and other desorption products showed that ZnO/TiO_2 is a promising system to be used as support or catalyst to H_2 production employed in fuel cells.

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Keywords: Zinc oxide; Titania; TPD; Methanol; Hydrogen production

1. Introduction

Fuel-cell powered vehicles using hydrogen are currently under extensive investigation. However, the use of hydrogen gas for vehicle applications is postponed by technical limitations associated with safety, storage and distribution [1]. Therefore, current trends indicate that vehicles equipped with fuel cells will use liquid fuels as hydrogen source, at least in the early stages of commercialization [2,3].

Methanol is potentially a good source of hydrogen, for the on-board production of hydrogen, due to its high hydrogen to carbon ratio, low boiling point and availability. The absence of carbon–carbon bonds in methanol drastically reduces the risk of coking. Methanol can also be produced from renewable resources and thus lowering the production of greenhouse gases [4].

The steam reforming of methanol has received much attention due to the ability to produce a gas with high hydrogen concentration while maintaining a high selectivity towards carbon dioxide. [3,5]. Fuels produced by steam reforming contain ≈70–80% hydrogen, those by partial oxidation ≈35–45%. Lower fractions of hydrogen in the fuel degrade fuel-cell performance. Steam reforming of methanol at moderate temperature (200–300 °C) mainly produces carbon dioxide and hydrogen, and only ~1–2%CO.

A proton exchange membrane (PEM) fuel cell can tolerate only minuscule quantities (10–20 ppm) of carbon monoxide in its feed. Brown [6] compares some advantages and disadvantages of various primary fuels suggested as hydrogen sources for PEM fuel cells. Methanol, natural gas, gasoline, diesel fuel, aviation jet fuel, ethanol, and hydrogen itself were evaluated in that work. He shows that all the other processes for creating hydrogen from organic-chemical fuels form large quantities of CO in their products, the amounts ranging from 10 to 25%.

Wasmus and Kuver [7] did a review about the development of the direct methanol fuel cell (DMFC), long being considered as the most difficult fuel-cell technology methanol crossover and catalytic inefficiency. In order to reduce the usage of precious metals they suggested that the best possible performance has to be extracted from a given amount of catalyst. This involves mainly catalyst preparation, pretreatment, electrode preparation and, in the case of supported catalysts, also the choice of a suitable support. Therefore, the

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doi:10.1016/j.cattod.2007.12.089

development of methanol decomposition catalysts for on-board production of hydrogen is highly required.

Copper and zinc-based catalysts were often used because Cu/ZnO-based catalysts are industrial low-temperature methanol synthesis catalysts. However, it has been shown that these catalysts present rapid deactivation in the methanol decomposition environment [8]. On the other hand, a number of recent studies concerning the ZnO-based catalysts characterization under oxidizing conditions have revealed that the mechanisms, formation of surface species, as well as, oxide phases synergy remain attractive for investigation in the steam reforming process [3,9]. Studies carried through by Agrell et al. [10], about the reduction of CO in the product of the steam reforming of methanol, had used commercial $Cu/ZnO/Al_2O_3$ catalyst. It was observed that the addition of oxygen in the steam–methanol feed mixture, as well as, the reduction of the contact time and decreases temperatures, minimizes the CO production.

The acid-basic properties of the ZnO/Al_2O_3 system had been characterized in the literature [11,12] as a function of the zinc oxide content and of the temperature of calcination. It was shown that the aluminate phase formation, for contents above of 20%, and the increase of the calcination temperature, from 600 °C up to 800 °C, had caused significant changes in the acidity and the basicity of the sample. The methanol oxidation product distribution reflects the nature of the surface active sites since redox, acid, and basic sites yield formaldehyde (HCHO), dimethyl ether (CH_3OCH_3), or CO_2, respectively; however, most pure metal oxides produce CO*x* above 200 ± C due to the decomposition of surface formate species. [13,14].

Spectroscopic studies of adsorbed methanol and temperature programmed desorption (TPD) analysis has been used to characterize oxides surface showing that surface methoxy and formate species are generated upon exposure of metal oxides (Al_2O_3, ZrO_2, TiO_2, NiO, Fe_2O_3, ZnO, CuO, MoO_3, CeO_2, Co_3O_4) to methanol vapor [14]. In a previous study of our group [15] using FTIR and TPD, it was concluded that the addition of ZnO to Al_2O_3 is responsible for the reduction of the strength and the number of the Brönsted acid sites and that the nature of these acid sites depends on the phases present on the catalyst.

The goal of this work is to evaluate the effect of the surface properties of a series of ZnO and TiO_2 supported catalysts using methanol as a probe molecule on temperature programmed desorption analysis. The characterization of its active sites can be helpful in choosing the most suitable catalyst to be applied in the methanol combined reform reaction (partial oxidation + -steam reforming), aiming to H_2 production for fuel cells.

2. Experimental

2.1. Catalyst preparation

- γ-Al_2O_3: (Harshaw—Al3996), (200 mesh), calcined at 550 °C for 5 h, under airflow.
- TiO_2: it was prepared by slow hydrolyze of titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$), dried at 120 °C for 19 h and calcined under air flow (60 ml/min) at 550 °C for 6 h.
- ZnO: it was obtained by slowly adding a 0.6 M Na_2CO_3 aqueous solution to a 0.6 M $Zn(NO_3)_2 \cdot 6H_2O$ aqueous solution. The precipitated was washed several times, dried at 100 °C and calcined under airflow at 500 °C for 6 h [12].
- 10% and 20%ZnO/Al_2O_3 (10ZnA, 20ZnA), 20%ZnO/TiO_2 (20ZnT) and 20%ZnO/20%TiO_2/Al_2O_3 (20ZnTiA): it was prepared by wetness-impregnation method, using $Zn(NO_3)_2 \cdot 6H_2O$. Calcination at 550 °C, 6 h under air flow.
- 20%TiO_2/Al_2O_3 (20TiA): it was obtained by wetness-impregnation technique, with ($Ti(OCH(CH_3)_2)_4$) under inert ambient. Calcination was carried out at 550 °C, 6 h under airflow. [16].

2.2. Catalyst characterization

- Superface area (BET method): it was determined by nitrogen adsorption at 77 K in Micromeritics equipment, ASAP 2000 model. The samples were pretreated under vacuum during the night at 300 °C.
- X-ray fluorescence (XRF): the testes were carried out in Rigaku instrument, RIX-3100 model, using Rh source, 50 KV and 80 mA.
- X-ray diffraction (XRD): the patterns were obtained with a Rigaku instrument Miniflex TG model, using Cu Kα radiation (30 KV e 15 mA). The step-scans taken over the range of 2θ from 10° to 90° in step of 0.05, the intensity data for each step was collected for 1 s. It was used ICDD-PDF-2 data for phase identification, by Hanawalt method.

2.3. Methanol temperature-programmed desorption (TPD-MeOH)

It was used a multipurpose unit equipped with an on-line quadrupole detector QUADSTAR 422 (QMS 200, Balzers). Initially the samples (100 mg) have been treated at 450 °C, under He flow (60 ml/min) for 1 h, at 10 °C/min and cooled down to room temperature (25 °C). At this temperature, He flow (60 ml/min) was switched and sent to Pyrex glass saturator that containing methanol at 25 °C. Then, the methanol vapor carried was introduced into the reactor for 30 min ensuring a saturated adsorption of methanol on the surface of catalysts. Afterwards, the catalyst was flushed with He (60 ml/min) for 30 min. TPD measurements were performed from room temperature to 800 °C at a heating rate of 10 °C/min with He as carrier gas. The desorbing species were monitored using the mass spectrometer. Multiple *m*/*e* ratios were collected during each TPD run. The ion/mass (*m*/*e*) signals with relative intensity monitored during the desorption had been: H_2: 2 (100%); He: 4 (100%); methane: 16 (100%), 15 (85.8%), 14 (15.6%); H_2O: 18 (100%); 17 (23%); 16 (1.6%); CO: 28 (100%), 12 (4.5%); N_2: 28 (100%), 14 (7.2%); methanol: 32 (66.7%), 31 (100%), 29 (69.4%); formaldehyde: 29 (100%), 30 (55%); CO_2: 44 (100%), 28 (11%), 16 (8.5%); dimethyl ether, DME: 45 (100%), 46 (61%), 29 (39%); methyl formate: 60 (38%), 31 (100%); dimethoxymethane, DMM: 75 (43.6%), 45 (100%), 29 (44%). Individual products were identified by their characteristic mass fragmentation patterns. The desorption

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