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Supported ZnO catalysts for the conversion of alkanes: About the metamorphosis of a heterogeneous catalyst

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Abstract
ZnO could be a suitable catalyst for the oxidative conversion of CH_4, C_2H_6 and C_3H_8. However, the main drawback is its thermal instability. Therefore, ZnO supported on ZrO_2, TiO_2, γ-Al_2O_3 and SiO_2 was investigated for the oxidative dehydrogenation of propane and ethane, and the oxidative coupling of methane. The stability of the supported ZnO is partially improved, but ZnO reacts with the support material, forming new compounds (Zn-zirconates, -titanates, -aluminates and -silicates), which already occurs below reaction temperature. This might also be the case for many other heterogeneous catalysts.

Key words
oxidative dehydrogenation; oxidative coupling of methane; oxidative dehydrogenation of ethane; oxidative dehydrogenation of propane; ZnO

1. Introduction

There are large resources of natural gas [1], therefore, an intense search for suitable catalysts for the conversion of natural gas is going on. The reactions of interest are:
1. Oxidative dehydrogenation of propane (ODP)

$$C_3H_8 + 1/2O_2 \longrightarrow C_3H_6 + H_2O$$

2. Oxidative dehydrogenation of ethane (ODE)

$$C_2H_6 + 1/2O_2 \longrightarrow C_2H_4 + H_2O$$

3. Oxidative coupling of methane (OCM)

$$2CH_4 + 1/2 \text{ or } 1O_2 \longrightarrow C_2H_{6\text{ or }4} + 1 \text{ or } 2H_2O$$

The oxidative dehydrogenation of propane and ethane is usually performed with transition metal oxides with flexible oxidation states (e.g. V, Mo, Cr) and it is rather well understood [2−5]. Cations without flexible oxidation states (MgO, CaO, SrO and BaO doped with Nd_2O_3) were also studied [6,7], showing the importance of defects created by the dopants.

In the co-feed mode, the oxidative coupling of methane is performed with metal oxides, in which the cations do not possess a flexible oxidation state [8]. Furthermore, the mechanism of the OCM is extremely complex and by far not understood [9,10]. An extensively studied catalyst is Li-doped MgO. However, a recent review showed that the knowledge on Li/MgO is very limited, despite the intensive research [10]. A detailed investigation of Li/MgO catalysts, prepared via different synthetic routes, performed by us showed that this catalyst suffered from an intrinsic instability and a strong and fast loss of Li, prohibiting any practical application [11].

In the search for suitable catalysts for the OCM, ZnO was also investigated for the oxidative conversion of lower alkanes [12–20]. It was reported to be a suitable catalyst. Li/ZnO as catalysts for the OCM was also studied and found to be suitable [13]. However, in a previous study indications were found that unsupported ZnO and Li/ZnO were unstable [20]. Due to the structural similarity to Li/MgO, it is reasonable to assume a strong and fast loss of Li, as it was found for Li/MgO [10,11].

Depositing a catalytic material on a support material is a common way to stabilize unstable catalysts. Choudhary et al. reported a reduced catalytic activity for supported Li/MgO and indications for a reaction of the catalyst with the support material [21]. However, detailed studies (catalytic activity

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and/or structure-activity relationship) of supported MgO or supported ZnO are missing in literatures. Therefore, in this work we investigated the possibility to stabilize ZnO via deposition on support materials (ZrO_2, TiO_2, γ-Al_2O_3 and SiO_2). The structure of these materials, the anticipated structural changes and the stability under reaction conditions were investigated in detail. The oxidative dehydrogenation of propane and ethane, and the oxidative coupling of methane were used as test reactions.

We would like to note that we did not try to find a better catalyst for the ODP, ODE and OCM, but we tried to improve the stability of ZnO by studying the structure of the catalysts and their changes using the above mentioned reactions as test reactions. We were also willing to accept a low catalytic activity of supported ZnO, as long as a stable material is obtained; because in a second step, the catalytic activity of a stable catalyst can be improved via doping, for an unstable catalysts doping cannot improve the stability.

2. Experimental

2.1. Catalyst preparation

A solution of $Zn(NO_3)_2$ (Fluka, $Zn(NO_3)_2{\cdot}6H_2O$, $\geqslant$99.0%) in deionised H_2O was added dropwise to the support material (the origin and specific surface area are shown in Table 1) and stirred until a thick paste was formed. The paste was dried at room temperature for 24 h and then heated, with a heating rate of 7.5 K/min, to 450 °C under air. The temperature was held at 450 °C for 3 h. The obtained material was crushed and sieved, and only the fraction below 200 μm was used for catalytic experiments. This preparation procedure was adapted from Chouillett and co-workers [22] and were applied for all the support materials, although in the original publication it was reported only for SiO_2.

Table 1. The origin and specific surface area of the used support materials

Support	Origin of support	BET surface area (m^2/g)
ZrO_2	Aldrich, 3 mol% Y stabilized	106
TiO_2	BASF, Ti11000E	126
γ-Al_2O_3	Alfa Aesar	105
SiO_2	BASF, D11−10	101

The ZnO loadings for each catalyst were 5, 10, 15 and 20 wt%. The loading was calculated according to Equation (1). Commercially, ZnO was obtained from Fluka with a purity higher than 99.0%.

$$\text{ZnO (wt\%)} = [\text{ZnO (g)}/\text{Support (g)}] \times 100\% \quad (1)$$

For the preparation of blank samples, the same preparation procedure was applied, except that H_2O was added without $Zn(NO_3)_2$. The calcination temperature of 450 °C was chosen, because it is the lowest applied reaction temperature. Calcination at higher temperatures could anticipate structural changes, which occurs anyway during the reactions at higher reaction temperatures.

2.2. Catalyst characterization

2.2.1. Atomic absorption spectroscopy

The Zn content of different samples was quantified via atomic absorption spectroscopy (AAS), using an AAS NovAA 400 G device from Analytik Jena via flame. A summary of the calculated and measured loadings is given in Table 2.

Table 2. The amounts of ZnO loading in prepared catalysts and in the catalyst bed

Catalyst	ZnO calculated (wt%)	ZnO measured (wt%)	Amount of catalyst[a] (mg)	Amount of ZnO[b] (mg)
ZnO	–	–	19	19
5 wt% ZnO/SiO_2	5	4	575	19
10 wt% ZnO/SiO_2	10	10	226	19
15 wt% ZnO/SiO_2	15	12	154	19
20 wt% ZnO/SiO_2	20	19	114	19
5 wt% ZnO/ZrO_2	5	3	584	19
10 wt% ZnO/ZrO_2	10	9	248	19
15 wt% ZnO/ZrO_2	15	13	165	19
20 wt% ZnO/ZrO_2	20	20	120	19
5 wt% ZnO/TiO_2	5	3	400	15
10 wt% ZnO/TiO_2	10	7	209	17
15 wt% ZnO/TiO_2	15	11	146	18
20 wt% ZnO/TiO_2	20	19	114	18
5 wt% ZnO/Al_2O_3	5	–	665	19
10 wt% ZnO/Al_2O_3	10	4	412	19
15 wt% ZnO/Al_2O_3	15	7	236	19
20 wt% ZnO/Al_2O_3	20	26	149	19
ZrO_2	–	–	100	–
TiO_2	–	–	100	–
Al_2O_3	–	–	100	–
SiO_2	–	–	100	–

[a] The amount of catalyst loaded into the reactor; [b] the resulting amount of ZnO in the reactor

2.2.2. N_2-adsorption

The specific surface area was determined by a Micromeritics Gemini III 2375 Surface Area Analyzer, using N_2-adsorption at −196 °C. Before measuring, the supported samples were degassed under 300 °C and 0.15 mbar for at least 30 min. Unsupported ZnO was outgassed at 120 °C. The surface areas were calculated following the method of Brunauer, Emmett and Teller (BET).

2.2.3. X-ray diffraction

The powder diffractograms were performed on a PANalytical X'Pert PRO MPD Diffraktometer instrument using Cu K_α radiation ($\lambda = 1.5418$) and a position sensitive-detector (PSD) in the 2θ range from 10° to 90° with 0.015° step.

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