Oxidation of methane to methanol and formaldehyde over Co–ZSM-5 molecular sieves: Tuning the reactivity and selectivity by alkaline and acid treatments of the zeolite ZSM-5 agglomerates

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ABSTRACT

Alkaline treatment of templated Na–ZSM-5 zeolites with NaOH solutions resulted in the creation of intercrystalline mesopores within the zeolite agglomerates, while preserving the micropore volume and crystallinity. It was found that the zeolite external surface area increased with increasing NaOH concentration and pretreatment time. These alkaline-treated samples were loaded with cobalt and a linear relationship between the number of cobalt oxidic species and the external surface area of the zeolite could be established. This in turn leads to a linear relationship between the ZSM-5 surface area and the amount of methanol produced over Co–ZSM-5 from methane and oxygen at 423 K. Attempts to remove extra framework alumina species by an acid treatment were successful. However, this acid treatment increased, after Co-deposition, the amount of highly dispersed Co^{2+} inside the ZSM-5 channels, which resulted in a higher selectivity towards formaldehyde. The nature of the charge-compensating cation also determined the cobalt speciation. Co–H–ZSM-5 samples contained more cobalt inside the channels and were more selective towards formaldehyde formation than Co–Na–ZSM-5 samples.

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1. Introduction

Cobalt-containing zeolites can potentially be applied in a wide variety of applications, such as the reduction of NO by hydrocarbons [1–8] and alkane ammoxidation [9–11]. Recently, we have shown that Co–ZSM-5 zeolites are able to oxidize methane to oxygenates [12]. Methane oxidation to oxygenates is one of the greatest challenges in heterogeneous catalysis. Fe–ZSM-5 is known to be active for this conversion although N_2O was indispensable as oxidant [13–15]. Due to the limited availability of N_2O the use of molecular oxygen or air as an oxidant is more attractive. Recently, it was reported that Cu–ZSM-5 [16,17] and Co–ZSM-5 [12] were able to perform the methane to oxygenates reaction, using oxygen as oxidant. Interestingly, the selectivity and activity of Co–ZSM-5 are determined by the cobalt speciation. Co–ZSM-5 prepared by ion-exchange with cobalt acetate and mainly containing highly dispersed cobalt species inside the zeolite channels, were selective towards formaldehyde. In contrast, impregnated Co–ZSM-5 samples, mainly containing cobalt oxidic species at the zeolite outer surface, were more selective towards methanol [12].

Unfortunately, the direct conversion of methane to methanol over Co–ZSM-5 zeolites is not (yet) a continues process, but consists of three steps: (1) formation of active species by calcination in air; (2) reaction of the active species with methane at low temperature (i.e., 423 K) and (3) extraction of the strongly adsorbed products, using a polar protic solvent [12]. Often zeolites for this process consist of small crystals agglomerated to larger entities of typically >2 μm [18,19]. This might hamper the accessibility of the active sites in the zeolite/zeolite aggregates and merits a more detailed investigation. Therefore, we have investigated the role of pore accessibility on the catalytic performance of Co–ZSM-5 zeolites for the production of oxygenates from methane and oxygen.

Accessibility of zeolites can be improved by introducing mesoporosity either during the synthesis or by post-synthesis treatments. During synthesis combustible hard templates can be used, such as carbon aerogel [20,21] or resorcinol–formaldehyde aerogels (RFAs) [22]. After zeolite synthesis these templates are removed with the concomitant formation of mesopores.

For post-synthesis treatments often steaming and acid leaching are applied, which is expected to lead to dealumination [23–26]. Unfortunately, dealumination of highly siliceous zeolites, such as ZSM-5, generally induces rather limited mesoporosity [19,27,28]. For those materials new post-synthesis treatment using alkaline solutions to introduce mesopores by framework Si extraction was developed [29–32,19]. It was shown that desilication usually results in controlled mesoporosity and does not affect micropore size nor acidic properties [33]. Groen et al. showed that desilicated ZSM-5 zeolites, followed by Fe deposition, were more active for N_2O decomposition as compared to the non-leached zeolites. This was ascribed to a higher amount of highly active Fe^{2+}-species present in the desilicated samples [34,35].

In the current work we have investigated the role of alkaline (NaOH) treatment on ZSM-5 agglomerates, still containing their template, on mesopore formation. The role of these mesopores on the speciation of cobalt and the activity of these Co-containing samples for methanol production from methane and oxygen is the main goal of the study. Different alkaline treatments were applied to vary the mesoporosity of ZSM-5 zeolites. The influence of mesoporosity on cobalt speciation was investigated by UV–Vis–NIR diffuse reflectance (DR) spectroscopy and Temperature Programmed Reduction (TPR) making use of hydrogen. The activity and selectivity towards methane activation was established in batch mode using a plug-flow gas-phase reactor system.

2. Experimental

2.1. Materials and treatments

Na–ZSM-5 from ExxonMobil (with Si/Al ratio of 17) with the template present in the pores was used as the starting material and will be referred to as ZSM-5-*p* (all sample names and treatments are compiled in Table 1). This material was alkaline-treated by stirring 2 g of zeolite in 90 ml of an aqueous solution of NaOH (Acros Organics, extra pure) with varying concentration (0.1 M and 1 M) at 343 K for different times (10–30 min). The sample was subsequently washed, dried and calcined to remove the template. The samples were denoted as ZSM-5-*at-A–B*, where *at* denotes "alkaline treated", *A* is the concentration of NaOH hydroxide and *B* the reaction time. In addition, ZSM-5-*p* was calcined in air at 823 K for 12 h to remove the template. Next, this sample was given an alkaline treatment by contacting 2 g of the calcined material in 90 ml of 0.1 M NaOH solution at 343 K for 30 min. This sample is named ZSM-5-*nt-at*-0.1–30 with *nt* denoting "no template" and the other suffixes are as described above.

ZSM-5-*p* and ZSM-5-*at*-1–20 samples were additionally acid-treated by using 0.1 M HNO_3 (Merck, 65% (for analysis grade)) at RT for 20 h. After acid treatment the samples were washed, dried and calcined at 823 K to remove the template. The samples were named ZSM-5-*acid* and ZSM-5-*at*-1–20-*acid*, respectively. In addition, to prepare the proton-exchanged ZSM-5-*p* and ZSM-5-*at*-1–20 these samples were three times ion-exchanged with NH_4NO_3 (Acros Organics, 99 + %) at 343 K for 12 h. After washing and drying the samples were calcined at 823 K. They are named *H*–ZSM-5-*p* and *H*–ZSM-5-*at*-1–20, respectively.

2.2. Characterization

Textural properties of the materials were studied by N_2 physisorption measurements at 77 K using a Micromeritics Tristar 3000. Prior to the adsorption measurements the samples were dried at 573 K for 12 h. The BET method was applied to calculate the total surface area. The *t*-plot method was applied to obtain the micropore volume and external surface area. The BJH model was used to determine the size of the mesopores.

Powder X-ray diffraction (XRD) patterns of the samples were measured using a Bruker-AXS D8 advance powder diffraction apparatus equipped with an automatic divergence slit (filtered Co-K_α radiation $\lambda = 0.179$ nm). Morphology and crystal sizes were determined by Scanning Electron Microscopy (SEM). SEM micrographs were obtained using a Philips XL30FEG electron microscope.

2.3. Co-loading and characterization

Co–ZSM-5 zeolites were prepared by incipient wetness impregnation using a 1.5 M cobalt nitrate solution (2 g zeolite, 0.5 ml solution, $Co(NO_3)_2 \cdot 6H_2O$, Acros Organics, 98%). After metal loading the samples were dried in air at 333 K. All sample names were similar as described above for the bare zeolites however now with the prefix "Co" (Table 1).

Cobalt loadings were determined by Atomic Absorption Spectroscopy (AAS) using a VARIAN Spectra AA-20 instrument. 10 mg of the Co–ZSM-5 zeolite was dissolved in 0.1 M HF to prepare the solutions for AAS measurements. Temperature Programmed Reduction (H_2-TPR) was performed on an Autochem 2920 instrument from Micrometrics. 0.8 g catalyst was loaded in the reaction and dried in Ar at 393 K for 1 h. After lowering the temperature to room temperature the Ar was replaced by 5% H_2 in Ar (50 ml/min) and the TPR was performed by heating the sample to 1173 K with a ramp of 5 K/min. To quantify the TPR data the recorded traces were deconvoluted using Gaussian peak shapes.

2.4. Combined activity and UV–Vis–NIR measurements

Methane activation measurements, in batch mode, and UV–Vis–NIR diffuse reflectance spectroscopy (DRS) experiments were simultaneously performed in a specially designed quartz reactor equipped with a UV–Vis–NIR transparent window [36]. Before reaction the samples (1.0 g, grain size 0.2–0.5 mm) were mildly calcined [37,38] in air (1000 ml/min) at 823 K (heating ramp of 0.5 K/min). After calcination the samples were cooled to RT and flushed with helium. Subsequently, the samples were heated to 423 K (heating ramp of 10 K/min) in methane (8% in He; 25 ml/min) and kept at that temperature for 25 min.

After reaction with methane the methanol and formaldehyde formed were collected by extraction. 0.2 g of the sample was stirred in 0.5 ml ethanol for 1 h. The product composition was

Table 1
Overview of the Co–ZSM-5 samples under investigation, including their cobalt loadings, sample codes and treatment procedures.

Entry	Bare zeolite sample[a]	Treatment	Co loading[b] (wt.%)
1	ZSM-5-*p*	No treatment	2.1
2	ZSM-5-*at*-0.1–30	0.1 M NaOH, 30 min, 343 K	2.0
3	ZSM-5-*at*-1–10	1 M NaOH, 10 min, 343 K	2.1
4	ZSM-5-*at*-1–20	1 M NaOH, 20 min, 343 K	2.2
5	ZSM-5-*nt-at*-0.1–30	ZSM-5 without template, 0.1 M NaOH, 30 min, 343 K	2.2
6	ZSM-5-*acid*	0.1 M HNO_3, 24 h, RT	2.2
7	ZSM-5-*at*-1–20-*acid*	(1) 1 M NaOH, 20 min, 343 K	2.1
		(2) 0.1 M HNO_3, 24 h, RT	
8	*H*-ZSM-5-*p*	Ion-exchange with NH_4NO_3, followed by calcination	2.0
9	*H*-ZSM-5-*at*-1–20	(1) 1 M NaOH, 20 min, 343 K	2.2
		(2) Ion-exchange with NH_4NO_3, followed by calcination	

[a] A prefix "Co" is used for the samples after Co-loading i.e., ZSM-5-*p* will be named than Co–ZSM-5-*p*.
[b] After Co loading using the incipient wetness impregnation method.