



The effect of iron loading and hydrothermal aging on one-pot synthesized Fe/SAPO-34 for ammonia SCR



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ABSTRACT

The current commercially-available technique for NO_x reduction for diesel engines is the selective catalytic reduction (SCR) of NO_x with NH₃ over Cu zeolites. One of the problems of this technique is their limited ability to convert NO_x at diesel particulate filter (DPF) regeneration temperatures. In addition, during regeneration of the DPF there is a risk of thermally deactivating the SCR catalyst. Thus, the aim of the current work was the development of a catalytic system that can reduce NO_x both at low as well as high temperature and in addition is stable at high temperature. In order to reach this goal, a Fe/SAPO-34 with chabazite (CHA) structure was combined in a system with a commercial Cu/CHA catalyst. Earlier studies have shown that it is difficult to ion-exchange Fe into CHA structures due to steric hindrance, and we have therefore used a novel synthesis procedure which incorporated iron directly into the zeolite structure. Fe/SAPO-34 with three different Fe-loadings (0.27; 0.47 and 1.03 wt.% Fe) were synthesized and the catalysts were characterized using inductively coupled plasma atomic spectroscopy (ICP-AES), N₂ adsorption-desorption isotherms, BET area measurements and X-ray diffraction (XRD). The chemical composition, porous and crystalline structure of the parent SAPO-34 sample were found to be only slightly affected by addition of small amounts of Fe in the framework zeolite structure. However, more visible changes in the crystallinity were observed in the Fe/SAPO-34 catalysts with higher Fe content, which were attributed to the unit cell size expansion provoked by integration of higher amounts of Fe into the zeolite SAPO-34 framework. The Fe/SAPO-34 with the lowest Fe-loading (0.27 wt.%) was found to be the best catalyst when considering activity as well as high temperature stability. The synthesized Fe/SAPO-34 catalyst demonstrated a significantly improved NO_x reduction performance at high temperatures (600–750 °C) when compared to a commercial Cu/CHA SCR system, and the combined system (Fe/SAPO-34 + Cu/CHA) exhibited a very good performance in a large temperature interval (200–800 °C) that encompasses most diesel exhaust gas conditions.

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1. Introduction

Increasing environmental concerns over the past several decades have resulted in the need to find innovative ways to deal with exhaust emissions produced by the lean combustion of fossil fuels. Achievement of high environmental standards for the emissions of nitrogen oxides (NO_x), unburned hydrocarbons and particulate matter (i.e., soot) from mobile and stationary sources remains an important challenge [1]. Thus, the need for better fuel economy, which diesel and lean burn gasoline engines possess,

and more stringent NO_x emission standards have driven the development of different strategies of NO_x reduction in oxygen rich conditions [2,3]. One of the most effective NO_x abatement technologies is the selective catalytic reduction (SCR) of NO_x by NH₃, which is used for stationary power plants, industrial processes and also for automobiles [2].

Many fundamental and more applied studies have been devoted to understand the basic mechanism of NH₃ SCR and to develop highly active and selective catalysts [4–6]. V₂O₅/WO₃ supported on anatase TiO₂ is one of the most commonly used and widely investigated SCR systems, for stationary applications [5,6]. In the last years, materials based on transition-metal ion-exchanged zeolites have received significant attention due to the improved NO_x reduction performance and thermal stability in a wide temperature range [2].

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Hence, different experimental and theoretical studies were focused on the effect of the metal (Cu, Fe, Ce, Co, and Ag) and type of the zeolites (ZSM-5, MFI, FER, BEA, SSZ-13, and SAPO-34) [4,7–9], on the stability and the overall SCR performance [7,9–12]. In general, Fe- and Cu- based zeolites are selected as the most active SCR catalysts for NO_x reduction [13,14]. In particular, it was found that the Cu-ion exchanged zeolites are characterized by superior low temperature activity [13,14]. On the other hand, Fe-based zeolites (mostly Fe/ZSM-5 and Fe/BEA) are known to be more active for SCR at higher temperatures ($\geq 400^\circ\text{C}$) [15–17]. Based on the effectiveness of the individual Fe/ZSM-5 and Cu/CHA based zeolites, recent studies showed that they could be combined in order to achieve high NO_x conversion over a broader temperature range [13,14].

However, there are several problems connected with using zeolites like ZSM-5 or BEA, like their relatively low hydrothermal stability, in combination with susceptibility towards hydrocarbon (HC) poisoning and coking [18–23]. This is the background for the development of a new class of hydrothermally stable small-pore zeolites, which have the chabazite (CHA) structure, and put into use on Ford U.S. diesel trucks in 2010 [24]. These Cu/CHA systems showed much better NO_x conversion efficiency and superior hydrothermal durability when compared to large (Cu/BEA or Cu/Y) or medium pore zeolites (Cu/ZSM-5) catalysts [10,12,25]. For example [26,27], silico-alumino-phosphate molecular sieves (SAPO) with chabazite related structures exhibited excellent stability of the framework at 1000–1200 °C. In addition the chabazite structure has a small pore radius ($\sim 3.8 \text{ \AA}$), which hinders the hydrocarbons (HC) from entering the pores, resulting in a resistance to HC poisoning and coking [28]. Many efforts have been devoted in the last few years to the development of an NH₃-SCR catalyst based on Cu/SSZ-13 (SSZ-13 is the silico-aluminate form of the CHA structure) or Cu/SAPO-34 (silico-alumino-phosphate form of the CHA structure) [10,12,25,29,30].

One of the problems for the practical application of the current commercially available Cu/CHA catalysts for NH₃ SCR on diesel vehicles is their limited ability to convert NO_x at filter regeneration temperatures in excess of 450 °C [22]. A promising solution to this is to combine Fe/zeolite with Cu/zeolite [13,14]. However, the use of Fe/BEA and Fe/ZSM-5 gives problems with hydrothermal stability and HC tolerance. Therefore it would be a large advantage to combine Fe/CHA with Cu/CHA, but there are issues with preparing Fe/CHA.

The conventional wet ion exchange is one of the most commonly used methods for preparation of Fe/zeolite catalysts, replacing the H⁺ or Na⁺ cations of the zeolite structure by ferric ions [31,32]. However, this technique is challenging for the synthesis of Fe-containing SAPO-34 or other chabazite-like molecular sieves, because of the small pore size ($\sim 3.8 \text{ \AA}$) of the zeolite matrices [28] and the larger ionic diameter [33] of the hydrated Fe³⁺ ions (9 Å). In a very recent work, an active Fe/SSZ-13 catalyst for NH₃ SCR was successfully synthesized by traditional aqueous solution ion-exchange method under the protection of N₂ [37]. The method used in the study was applied to prevent Fe²⁺ ions from being oxidized to bulky Fe³⁺ moieties (e.g., Fe(OH)) that can hardly penetrate into zeolite pores. It was demonstrated that the small pore CHA structure does not impede Fe²⁺ ion exchange and the formed Fe species become active at temperature above 400 °C after aging of the Fe/SSZ-13 catalyst. For potential practical applications, the authors suggested that Fe/SSZ-13 may be used as a co-catalyst together with Cu/CHA as integral after treatment SCR catalysts on the basis of the stable high temperature activity after hydrothermal aging [37]. Further, there exist a few studies in the literature addressing the hydrothermal synthesis of Fe/SAPO-34 catalysts, directly incorporating Fe into the structure, for the applications of chloromethane transformation to light olefins and of methanol conversion [34,35]. In a recent patent application, NH₃ SCR of Fe/SAPO-34, with Fe incorporated

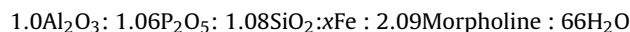
into the structure, was studied, but only up to 500 °C [36]. However, there are today no studies available that use one-pot synthesized Fe/SAPO-34 for NH₃ SCR in a broad temperature interval.

The objective of our work is therefore to use the novel synthesis method for incorporating the iron directly into the CHA structure during the zeolite synthesis. We have thereafter combined this Fe/SAPO-34 with Cu/CHA in a catalyst system and received high activity over a broad temperature interval (200–800 °C). A series of Fe/SAPO-34 catalysts with different Fe loadings (0.27, 0.47, and 1.03 wt.% Fe) were prepared by Fe incorporation directly in the SAPO-34 synthesis [38], adopted from the original method for pure SAPO-34 described by Prakash and Unnikrishnan [39]. Then, a combination of several characterization techniques was applied, such as inductively coupled plasma atomic spectroscopy (ICP-AES), N₂ adsorption–desorption isotherms, surface area measurements, and X-ray diffraction (XRD). In addition, to quantify the effect of the hydrothermal aging of the Fe/SAPO-34 and a commercial Cu/CHA SCR catalyst, multiple long-term and accelerated aging protocols were carried out by varying thermal treatment temperatures (800–900 °C) and time (1–80 h) of aging. For fresh and hydrothermally aged samples NH₃-storage/temperature-programmed desorption (TPD), ‘standard’ and ‘rapid’ NH₃ SCR were performed.

2. Experimental

2.1. Fe/SAPO-34 catalyst synthesis

The preparation of the Fe/SAPO-34 catalyst in the present study and in our patent application reported in Ref. [38] followed the procedure of hydrothermal synthesis in which the transition metal substituted SAPO material was prepared directly from a gel, adopted from the original method for synthesis of pure SAPO-34 described by Prakash and Unnikrishnan [39], with the following molar composition:



where x is the *mol* concentration of Fe, varied by changing the amount of Fe(III) nitrate nonahydrate precursor.

In a typical synthesis, the first step is to prepare a solution of ortho-phosphoric acid (H₃PO₄, 85 wt.%, Merck) dissolved in milli-Q water, which was stirred for 15 min at room temperature. Then, pseudoboehmite (74% Al₂O₃, PURAL SB-1, Sasol) was slowly added (within 2 h) to the diluted phosphoric acid solution. The slurry was stirred at room temperature for 12 h until a uniform gel was obtained. In the second step, iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, Sigma–Aldrich), separately dissolved in 10 ml H₂O, was dropwise added to the slurry (within 1 h) and stirred for 30 min. In the third step, a solution of colloidal silica (LUDOX AS-40, SiO₂, 40 wt.% in H₂O, Aldrich) and morpholine (tetrahydro-1,4-oxazine, Sigma–Aldrich) were separately prepared and after complete dissolution (within 10–15 min), the silica-morpholine containing mixture was under constant stirring slowly added (within 1 h) to the first alumina-P-Fe-containing solution at room temperature. Next, the slurry was continuously stirred for 7 h under ambient conditions. The obtained reaction mixture was aged at room temperature for 24 h without stirring. Then, the solution was transferred into a Teflon-lined stainless steel autoclave, sealed and heated for 72 h at 200 °C. The crystallization process was carried out under autogenic pressure without stirring. The crystallization time was recorded from the start of heating of the autoclave in the oven, which was pre-heated to 200 °C. After cooling to room temperature, the liquid phase was separated from the solid phase and the crystalline product was centrifuged, thoroughly washed with distilled water and dried at 100 °C for 12 h. Finally, the result-

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