Selective Catalytic Reduction of NO by Ammonia Using Mesoporous Fe-Containing Zeolite Catalysts: An Option for Automotive Applications

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Introduction

Traditional three-way catalysts that can eliminate CO, hydrocarbons, and NOx simultaneously are effective for gasoline-powered engines, but do not work for diesels vehicles, since diesel engines are operating under oxygen-rich conditions where NOx reduction cannot be achieved easily. For both heavy-duty trucks and passenger cars some catalytic process is most possibly required. As an option, NO Selective Catalytic Reduction (SCR) with ammonia can be considered as a promising alternative since it could operate with oxygen-rich exhausts.

Even though vanadia based catalyst are very active in NO SCR with ammonia and have been commercialized, challenges still remain, e.g. concerns about the toxicity of vanadia and the low selectivity of the process at higher temperatures due to competitive NH_3 oxidation. In view of these challenges, the recent discovery of the remarkable activity of over-exchanged Fe-ZSM-5 catalysts in the SCR of NO with isobutene [1] and ammonia [2] was considered a breakthrough. However, due to the complicated procedure for the preparation of ion-exchanged catalysts the large-scale utilization of these catalysts in industry is not expected to be straight-forward. Another important problem which should be taken into account is a transport phenomenon since diffusion in ZSM-5 zeolite with channels dimensions within the range of small molecules would often limit the activity of the catalysts. A possible strategy to solve this problem can be the introduction of mesopores into the zeolite structure. In this work we has shown that by use of very simple impregnation procedure and subsequent high temperature preactivation it is possible to obtain very active SCR catalysts, which are even more active than reference vanadia based catalyst at higher temperatures.

Materials and Methods

The mesoporous ZSM-5 zeolite material with Si/Al=50 was synthesized by crystallizing the zeolite around a carbon matrix which was subsequently removed by combustion, according to the procedure described in [3]. Conventional ZSM-5-type zeolite with Si/Al=50 was prepared by the standard procedure [4]. Fe-containing HZSM-5 catalysts were prepared by incipient wetness impregnation of the H-form of the zeolite (fraction 0.18-0.295 mm) with an aqueous solution of iron nitrate. The impregnated samples were dried at room temperature for 2 hours followed by calcination at 450° C for 4 hours. All samples were characterized by XRD, SEM, NH_3-TPD, nitrogen adsorption measurements, and tested in the NO SCR with ammonia. The influence of different preactivation conditions on the catalytic activity was studied. Results were compared with traditional 3 wt% V_2O_5/TiO_2 catalyst.

Results and Discussion

A series of mesoporous and conventional Fe/HZSM-5 catalyst with different iron content was prepared using simple impregnation procedure. It was shown (Fig 1a) that for the catalysts with similar Fe content activity of mesoporous samples in NO SCR with NH_3 is significantly higher than for conventional samples, especially at high reaction rates, which can be explained by the better diffusion of reactants and products in the mesopores and better dispersion of iron particles in mesoporous zeolite as was confirmed by SEM analysis.

The influence of different pretreating conditions on the catalytic activity was also studied and it was found that it is possible to increase SCR performance significantly by preactivation in 1%NH_3/N_2 mixture at 500°C for 5 hours. After preactivation, the activity of mesoporous 6 wt% Fe/HZSM-5 catalyst is comparable with those of traditional 3 wt% V_2O_5/TiO_2 catalyst used as a reference at temperatures below 400°C and even more active at higher temperatures.

Significance

The results of this study show that by use of very simple impregnation procedure and subsequent pretreatment it is possible to obtain active SCR catalysts, which can be used as an alternative to the traditional vanadium-based catalysts.

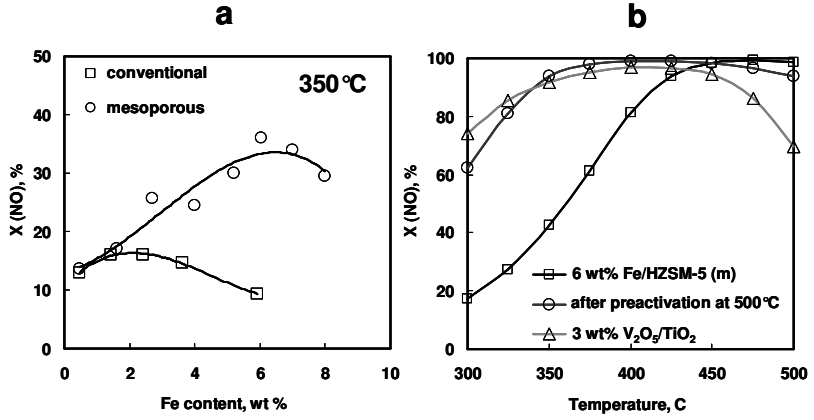

Figure 1. Effect of Fe loading (a) and pretreating in 1%NH_3/N_2 mixture at 500°C (b) on NO conversion over conventional and mesoporous Fe/HZSM-5 catalysts

References

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