BEA zeolite modified with vanadium as effective catalyst for selective reduction of NO with ammonia

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Introduction

Due to a high chemical and a thermal stability the transition metal containing zeolites are known as the promising catalysts of the removal of NO_x from outgases at high temperature range (over 673 K). Despite of the numerous publications on transition metal based zeolites the nature of the active sites is still a matter of discussion. Several kinds of metal sites have been introduced into zeolites such as isolated lattice and extra lattice metal species, metal oligomers, metal clusters and metal oxides [1].

In this work the V_xSiBEA zeolites were prepared by two-steps postsynthesis method which allowed to control the preparation condition and obtained catalysts with vanadium single sites incorporated into zeolite framework [2, 3]. Such prepared material is unique due to its high thermal stability, high level of metal dispersion and very well determination of its active sites. The zeolite catalysts obtained in this way were characterized and used in SCR of NO with ammonia as reducing agent.

Materials and Methods

A tetraethylammonium BEA (TEABEA) zeolite with atomic Si/Al ratio of 17 provided by RIPP (China) was dealuminated by a treatment with nitric acid solution (c = 13 mol dm^{-3}) at 353 K for 4 h to obtain the dealuminated BEA zeolite, labelled SiBEA, with atomic Si/Al ratio of 1141 and then washed several time with distilled water and dried at 368 K overnight. Then, obtained material was contacted with an aqueous NH_4VO_3 solution in excess at pH = 2.7 and stirred for 24 h at 298 K. Then, the suspensions were stirred in evaporator under vacuum of a water pump for 2 h in air at 333 K until the water was completely evaporated. As obtained vanadium containing samples were labeled V_xSiBEA with x = 1 – 7.5 V wt %.

The catalysts were characterised by diffuse reflectance UV-Vis, FTIR, XRD, ^{51}V MAS NMR and TPR

The activity of V_xSiBEA catalysts in SCR of NO with ammonia was measured in a conventional glass flow reactor. The composition of reaction mixture was: 1000 ppm NO, 1000 ppm NH_3, 3.5 vol.% O_2 and He as balance. The total gas flow was 0.1 L min^{-1} with the catalysts mass of 0.2 g. Before the catalytic tests the samples were pretreated at 798 K for 1 h in oxygen/helium mixture (0.1 L min^{-1}).

Results and Discussion

SiBEA support shows very low activity in SCR process with NO conversion lower than 15% in the whole temperature range. The introduction of vanadium in the SiBEA framework led to a considerable increase in NO conversion (**Fig 1A.**). For catalysts containing predominantly isolated pseudotetrahedral V(V) species ($V_{1.0}SiBEA$ and $V_{1.4}SiBEA$) activity increased with temperature with maximum conversion of 74 % at 773 K. For $V_{3.0}SiBEA$ catalyst with the mixture of framework pseudotetrahedral and extraframework polymeric V(V) species decrease in NO conversion in the high temperatures is observed. For catalyst containing large amount of vanadium oxide species ($V_{7.5}SiBEA$) a very sharp decrease in activity in SCR reaction at range 723 – 773 K is observed. This phenomenon is probably related to a competitive reaction of ammonia oxidation as well as deactivation of catalysts due to agglomeration of VO_x species in zeolite structure [4].

The application of $V_{1.0}SiBEA$ and $V_{1.4}SiBEA$ which contains predominantly pseudotetrahedral V(V) species lead to very low formation of N_2O (**Fig 1B.**). Thus, it may be concluded that presence of mononuclear framework vanadium sites has a very positive influence on selectivity and activity in SCR process.

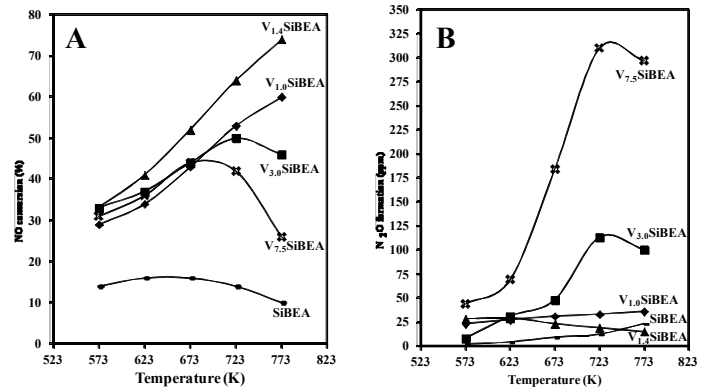

Figure 1. (A) temperature-dependence of NO conversion and (B) temperature-dependence of N_2O formation in SCR of NO with ammonia on V_xSiBEA catalysts

Significance

The V_xSiBEA zeolite catalysts, containing vanadium as pseudotetrahedral V(V) species have not only very high selective to desired product (N_2) but they are also very active in NO conversion at 773 K.

The catalytic activity of V_xSiBEA in SCR of NO with ammonia as reducing agent strongly depends on nature and environmental of vanadium in BEA structure.

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