



Conditions in which Cu-ZSM-5 outperforms supported vanadia catalysts in SCR of NO_x by NH₃

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Abstract

Continuous flows of a standard reactant mixture, featuring 0.6% nitric oxide, 0.6% ammonia and 3.3% oxygen at moderate space velocities over 4 different catalysts, have been used to compare relative activities for selective catalytic reduction of NO_x at 373–773 K. The catalysts tested were: Cu-ZSM-5 featuring >100% ion-exchange; a conventionally prepared vanadia-titania-tungstate (VTT) material and two unconventional catalysts prepared by vanadia deposition onto ex-sol-gel WO₃-TiO₂ supports. At catalytic temperature 473 K, higher conversion to N₂ was achieved over Cu-ZSM-5 than over the other three materials. Tests without NO at 473 K showed insignificant contributions to N₂ formation from ammonia oxidation over any of the catalysts, whereas tests at 573, 623, 673 and 773 K revealed larger progressive increases in such contributions over Cu-ZSM-5 than over the other catalysts. Values for SCR activities corrected for such contributions demonstrated that activity of Cu-ZSM-5 for SCR conversion of the standard NO + NH₃ + O₂ reactant mixture to N₂ at 473 K was ca. twice as great as the other three catalysts at that temperature, but that increasing the reaction temperature to 573 K caused only a slight further increase. 'Corrected' SCR activities in the standard reactant mixtures were rather similar for all four materials at 573 K, but with Cu-ZSM-5 marginally out-performed by one of two unconventional catalysts featuring vanadia upon an ex-sol-gel WO₃-TiO₂ support having tungsten incorporated into the TiO₂ anatase structure. Both of these unconventional catalysts outperformed a conventional 'VTT' catalyst. Observations upon variations in conversion to N₂ with variation in the oxygen content of the reactant gas mixture from 1 to 6% established another unique feature of the Cu-ZSM-5 catalyst at 473 K, viz. the need for ca. 4.5% O₂ to raise conversion to the maximum attainable over that catalyst at this temperature. No deactivation was observed after short-term runs at temperatures up to 823 K. Introduction of water vapour into the standard reactant mixture slightly enhanced the activity of Cu-ZSM-5 at 473 K.

Keywords: Ammonia; Copper-ZSM-5; NO_x reduction; Vanadia; Zeolites

1. Introduction

For efficiency/economic reasons, stationary power sources, such as electricity generating plants, operate in 'lean' conditions with an air-to-fuel ratios higher than

that stoichiometrically required. Emissions, thus, have a net-oxidising character with the result that potentially useful catalysts for removal of NO_x pollutants therein must be capable of selective catalytic reduction (SCR) of the NO_x — by an added reducing agent such as ammonia — whilst not significantly catalysing reduction of O_2 . [1,2]. The VTT catalyst commercially utilised for this purpose is a vanadia-tungsten oxide-titania mixture in which the V_2O_5 layers deposited upon WO_3 - TiO_2 are thought to provide active sites for the SCR process, e.g. with ammonia adsorbing onto V-OH sites and NO reacting with this adsorbed ammonia [2,3]. Vanadia-related sites considered important in the vanadia-tungstate-titania (VTT) catalyst include acidic V-OH sites, plus redox sites capable of undergoing $-\text{V}=\text{O}$ to $-\text{V}-\text{OH}$ transitions. According to Chen and Yang, functions of the WO_3 deposit include: broadening the reaction temperature window; enhancing the poison resistance towards alkali metals; lowering the ammonia oxidation activity and increasing the acidity of the catalyst [3]. The present work includes results from studies to determine whether SCR activity and other properties of VTT materials are sensitive/insensitive to the incorporation of WO_3 throughout the titania support as distinct from surface-deposition.

Catalysts prepared by ion-exchanging copper ions for protons of the narrow-channel zeolite aluminosilicate H-ZSM-5 are usually denoted by Cu-ZSM-5. The very extensive R&D attention devoted to such materials in relation to NO_x removal from emissions to atmosphere from stationary or mobile power sources stems from evidence that, within differing experimental conditions, they may display limited catalytic activity not only for the selective reduction reaction with ammonia and urea [4], or with C_1 - C_5 hydrocarbons [4–10], but also for dissociation to N_2 and O_2 [11–13]. Considerations of Cu-ZSM-5 materials in the present paper will, however, be limited to activity for SCR with NH_3 and how this compares with that of VTT materials.

Qualitative similarities between the two types of material might be anticipated on the twin basis that vanadium and copper can each exhibit variable-valency, and that acidity of the titania or aluminosilicate support would in each case be modified by addition of the promoter elements. Initial objectives of the present study were (i) to test for the levels of SCR activity in converting ($\text{NO} + \text{NH}_3 + \text{O}_2$) to N_2 at temperatures 473–773 K over aliquots of Cu-ZSM-5 catalyst, and (ii) to compare them with activity over a conventionally prepared VTT catalyst. During the course of the research a paper by Komatso et al. appeared reporting rather small activity of Cu-ZSM-5 at 473 K either for SCR towards ($\text{NO} + \text{NH}_3 + \text{O}_2$) reactants or for ammonia oxidation [14]. However, the concentrations of NO and NH_3 reactants used in that study were each a factor of six less than employed in the present study with resultant large decrease in probability for bimolecular reaction events between adsorbed species derived from NO or NH_3 respectively. Results reported here represent much more promising levels of SCR activity over Cu-ZSM-5 at 473 K. Also presented here are results of comparative measurements upon SCR activity attained over catalysts prepared by depositing vanadia onto novel ex-sol-gel (WO_3 -

TiO₂) supports. Incorporation of 5 or 10% WO₃ into the TiO₂ lattice of these materials is demonstrated by XRD together with stabilization of the TiO₂ (anatase) structure to temperatures of ca. 1173 K [15]. The anatase structure had been reported to increase the amount of V=O species on the surface of TiO₂-supported vanadia catalysts by favouring precipitation of favourable crystallographic structures at the anatase/V₂O₅ interface [16].

2. Experimental

2.1. Materials preparation and characterizations

The introduction of copper ions to increasing extent into a H-ZSM-5 material having Si/Al ratio = 13.4 was achieved by repeated ion exchange with aqueous solutions containing 0.05 M copper acetate. After drying in a vacuum oven at 383 K, the ion-exchanged materials were calcined in O₂ at 773 K for 2 h. Copper contents of materials thus prepared were determined by acid digestion and AA analysis which showed that 2.4% copper was the highest loading achieved. The designation Cu-ZSM-5 herein means that material, unless otherwise indicated. A VTT material of the type used commercially with 8% WO₃ and 4% V₂O₅ was prepared following the procedure described by Chen and Yang [17] which involved co-impregnation of an aqueous oxalic acid solution containing ammonium metavanadate and ammonium metatungstate onto predensified titania. The material was dried in vacuum at 383 K for 15 h and subsequently calcined for 20 h at 773 K in an O₂ flow. Sol-gel procedures were adopted to achieve the preparation of novel WO₃-TiO₂ supports having five or ten atom-percent of tungsten incorporated into titania [15]. After drying in vacuum and calcination at 773 K for 4 h, deposition of 4% vanadia thereon was achieved by wet impregnation with an oxalic acid solution of V₂O₅ followed by vacuum drying and calcination in O₂ at 773 K for 16 h. These 4% vanadia on 5% WO₃-TiO₂ or 10% WO₃-TiO₂ materials are hereinafter designated as Sample A and Sample B respectively.

Characterization of the relative ease of reducibility of the vanadia or copper upon or within the 'as-prepared' materials were achieved by a conventional temperature programmed reduction (TPR) procedure using 3% H₂ in argon, and a linear temperature ramp of 10° min⁻¹. Powder X-ray diffraction (XRD) patterns from the 'as-prepared', ex-sol-gel WO₃-TiO₂ materials were collected at ambient temperature for microstructural characterizations using a Philips MCD diffractometer featuring optoelectronic control to ensure precise measurements of θ values. Peak width positions and areas were evaluated by computer fitting of profiles. Effects of increasingly severe calcination upon microstructure of these materials were also investigated.

2.2. Tests for SCR activity

Small (25 or 10 mg) aliquots of the 'as-prepared' materials were supported upon a quartz fritted disc fused within a quartz microcatalytic reactor, either alone or admixed with silicon carbide. Two separate inlet tubes to the reactor respectively carried ammonia alone and a suitable premixed gaseous mixture of nitric oxide and oxygen in helium carrier gas. Flow rates from cylinders of 3%NO/He, 3%NH₃/He, 10%O₂/He and high-purity helium were adjusted by mass-flow controllers to deliver to the sample at total flow rates of 30 or 60 ml min⁻¹, a standard reactant gas mixture having a targeted composition of 0.6%NO + 0.6%NH₃ + 3.33%O₂. Tubing from the reactor exit to the gas sampling valve and thence to the GC for analysis was heated to avoid deposition of ammonium compounds. Addition of water vapour as an extra component in the gaseous reactant flow reaching the sample was, when so desired, introduced directly into the reactor from a motorized syringe and vapourised therein to achieve selected partial pressures in the reactant flow. Studies on oxygen dependence were carried out in the same system by using the O₂ and He flow controllers to achieve different partial pressures of O₂ while keeping constant the overall space velocity and partial pressures of NO and NH₃.

3. Results

3.1. Material characterizations

XRD

Fig. 1B illustrates a series of XRD patterns obtained from the ex-sol-gel 5 atom-% WO₃-TiO₂ support material after calcination at 673 K (bottom patterns), and also after 2 h calcinations at 773, 873, 973, 1073 K. With the exception of that for the 1073 K-calcined sample, the only difference apparent between the other 4 XRD patterns is some narrowing of diffraction peaks — consistent with TiO₂ particle growth, but no change in an anatase crystal structure of the WO₃-TiO₂ material. Fig. 1A presents a series of XRD patterns measured upon an ex-sol-gel TiO₂ powder obtained by similar preparation, but without WO₃. The patterns in the two lower XRD's exactly correspond to that for TiO₂ in its anatase crystal form and furthermore are identical to the bottom four XRD's shown for WO₃-TiO₂ in Fig. 1B. From this identity it may be concluded (i) that the WO₃-TiO₂ material had the TiO₂-anatase crystal structure, which it retained even after calcination up to 973 K, and (ii) that no XRD evidence was found for any WO₃-related phase after those calcinations. The topmost plot of Fig. 1B does, however, show evidence for segregation of a WO₃-related phase after calcination at 1073 K, but even then the TiO₂ component apparently retained the TiO₂ anatase structure. No comparable retention of the anatase structure was shown by the tungsten-free ex-sol-gel TiO₂ material, since the 2θ plot in Fig. 1A after 873 K calcination already demonstrated predom-

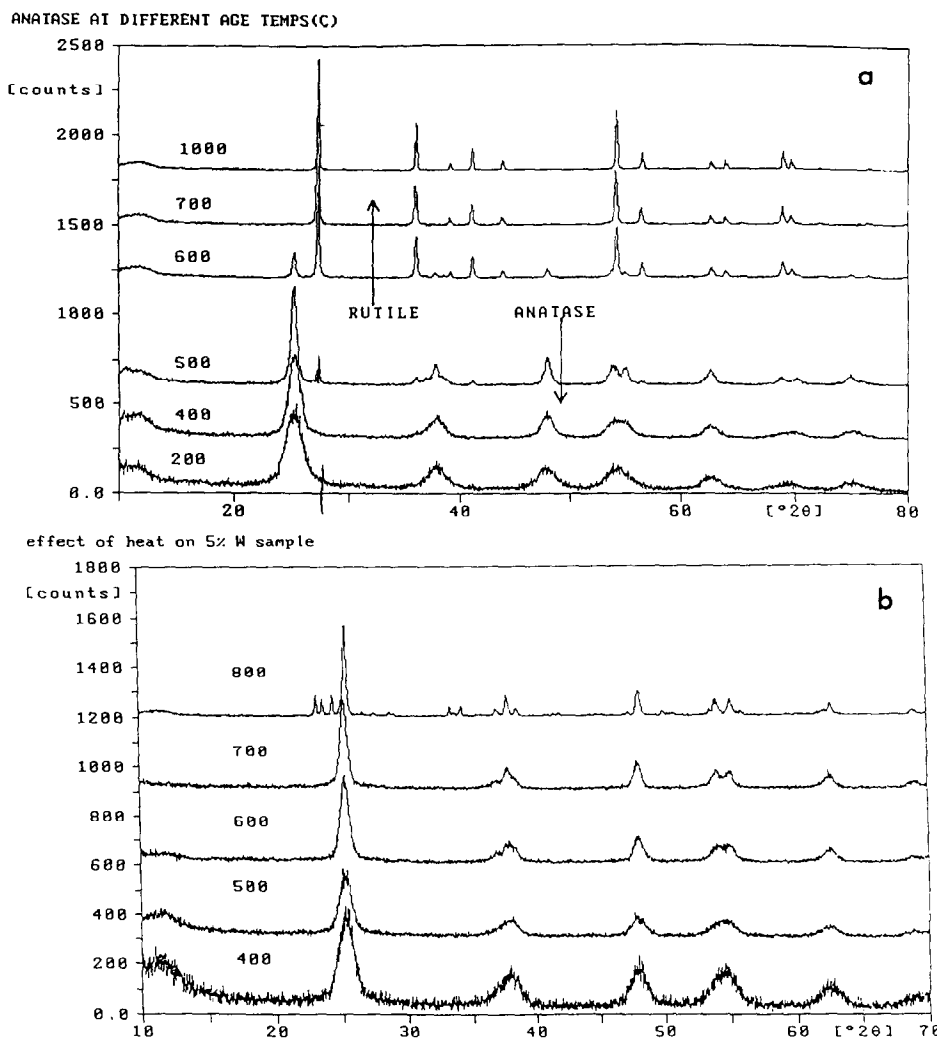


Fig. 1. XRD patterns after oxidation for 2 h at the indicated temperatures: (1a) for TiO_2 ex-sol-gel, and (1b) for 5% WO_3 - TiO_2 ex-sol-gel.

inance of the TiO_2 -rutile structure. Indeed features characteristic of rutile are already detectable even after calcination at 773 K.

TPR

Plots (a), (b), and (c) of Fig. 2A summarise TPR profiles measured in identical conditions upon aliquots of the three oxide-supported vanadia catalysts after in-situ preoxidations in flowing O_2 at 773 for 2 h followed by cooling in O_2 and brief flushing in 3% H_2 /Argon before commencing temperature ramp at 10°min^{-1} . Plot (c), which was obtained for a VTT sample with the same nominal 4% vanadia as the others, — but had been prepared by deposition on top of tungstate previously dispersed upon TiO_2 rather than within it — shows TPR features much smaller and

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