Vapour phase ammoxidation of mesitylene to 1,3,5-tricyanobenzene on V–Sn–O catalysts[☆]

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A series of vanadium–tin mixed oxide catalysts have been prepared by the solid-state reaction of V_2O_5 and SnO_2 at 1250°C. The fresh and the used catalysts have been characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). High temperature oxygen chemisorption (HTOC) has been employed to titrate the coordinatively unsaturated vanadia sites. Ammoxidation of mesitylene has been carried out on these catalysts and an optimum composition of vanadium is arrived at. Better yields of tricyanobenzene (TCB) compared to literature values are obtained. A good correlation between the oxygen uptake and the TCB yield extends the applicability of HTOC to the fused oxide system.

Keywords: vanadium–tin oxide fused oxide system; mesitylene ammoxidation; high temperature oxygen chemisorption

1. Introduction

Vapour phase ammoxidation of mesitylene to TCB is an important industrial reaction considering the vast potential for the product as an intermediate in the production of epoxy resin adhesives and anti-inflammatory compounds. The literature on this subject is largely patented with only a few published papers [1–3]. Reacting mesitylene with ammonia and oxygen (or air) generally leads to incomplete methyl–cyano transformation with the formation of a mixture of 1-cyano-3,5-dimethyl benzene, 1,3-dicyanotoluene and TCB, the compositions of which vary with the catalysts and the process conditions employed. Thus, selective production of TCB by the vapour phase process is very significant, in view of its low yield (< 20%) reported in the literature [1]. This leaves a lot of scope for the development of suitable catalysts.

Vanadia based catalysts have been extensively used for the selective oxidation and ammoxidation of hydrocarbons. The vanadium–tin oxide system (V–Sn–O) is particularly proven to catalyse several oxidation reactions like propene to acrylic aldehyde [3] and in the ammoxidation of picolines [4,5]. The ease with which oxygen is released due to the weakening of the vanadium–oxygen bond induced by the presence of tin, and its ability to activate molecular oxygen makes the V–Sn–O system highly selective for the ammoxidation reactions [6]. In a recent publication Bordoni et al. [7] have discussed the nature of vanadium species in this system very elaborately. In the present investigation a series of vanadium–tin oxide catalysts have been prepared with the vanadium content in the range (V/(V + Sn)) at% of 20–70. The unused and used catalysts have been characterized by XRD and FTIR. The fused V_2O_5–SnO_2 system has been used to study the title reaction focussing the attention on change in the yield of TCB as a function of vanadium content. Applicability of HTOC for characterizing the vanadia species in the fused vanadium–tin oxide system is also verified.

2. Experimental

V–Sn–O catalysts were prepared by the solid-state reaction, in air, of mixtures of powdered vanadium pentoxide and tin oxide (Loba Chemie, G.R. grade, India) of various ratios, at 1250°C for 3 h. In the present investigation, the vanadium content of the catalysts (expressed as atom percent (at%) of V in a mixture of V and Sn) was in the range 20–70%. After cooling quickly to room temperature (in about 40 to 60 min), the catalyst mass was crushed and sieved to 18–25 mesh (BSS) for studying the activity. XRD patterns were obtained on a Philips 1051 diffractometer using Ca K_α radiation. Infrared spectra were recorded on a Nicolet 740 FTIR. The KBr disc method was used. Surface areas of the catalysts were determined using a conventional volumetric high vacuum glass apparatus by the adsorption of nitrogen at −196°C. HTOC was also carried out in the same apparatus following the procedure according to Oyama et al. [8]. In a typical experiment, the catalyst was first reduced in a stream of pure hydrogen (35 $cm^3\ min^{-1}$) at 367°C for 4 h and evacuated at the same temperature for 2 h. The first oxygen adsorption isotherm was generated at 367°C. Keeping the samples at the same temperature the catalyst was then evacuated for 1 h and a second oxy-

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gen adsorption isotherm was generated. The difference between the parallel portions of the two isotherms was taken as the oxygen uptake.

Ammoxidation of mesitylene was carried out at atmospheric pressure in a 300 mm long, 15 mm i.d. glass tubular reactor provided with a concentric thermowell of 6 mm o.d. About 4 g of the catalyst was positioned between two quartz plugs and was maintained at the required temperature using PID controllers. The catalyst was initially reduced in hydrogen flow ($cm^3\ min^{-1}$) at 500°C for 2 h. Ammonia, air and mesitylene were used in the molar ratio of 3 : 20 : 1 respectively. Mesitylene was admitted into the reactor by means of a metering pump (B. Braun, Germany) at a flow rate of 2.5 cm^3/h. Water vapour was not used as a co-reactant. The reaction was studied in the temperature range 340–360°C. After allowing the catalyst to attain steady-state over a period of 30 min the product was collected for 5 min and analysed by gas chromatography separating it on an OV-17 column (2 m long and 3 mm dia) using an FID detector.

3. Results and discussion

X-ray diffractograms of the unused catalysts are shown in fig. 1. The patterns indicate the presence of crystalline V_2O_5–SnO_2. No other compound is identified. Change in intensities with increase in vanadia content can be noted. The weak diffraction lines of V_2O_5 intensified while the strong SnO_2 lines have become weaker. Surface areas of all the catalysts are generally low, recording less than 2 $m^2\ g^{-1}$. FTIR spectra of the unused catalysts recorded in the 600–1200 cm^{-1} range are shown in fig. 2. All the spectra show a prominent peak at 1018 cm^{-1} whose intensity has increased upto a V content of 57 at% and then onwards decreased.

Studying the structural dynamics of V_2O_5–$1.5SnO_2$ catalyst, Andersson [5] also has observed crystalline V_2O_5 and SnO_2 from the XRD patterns of his catalyst prepared by solid-state reaction in air at 1250°C. Though the possibility of reduction of V_2O_5 in its molten state cannot be ruled out [9], no reduced phases of V_2O_5 have been detected by the XRD analysis of the unused catalysts. This is also in perfect agreement with the observations of Andersson [4]. The FTIR spectrum of pure V_2O_5 is reported to exhibit peaks at 1025, 968 and 818 cm^{-1}. These can be attributed to the stretching vibrations of the short V=O bond, the V=O stretching bond and the stretching vibrations of the longer V–O bond respectively [5]. The shift in the position of the peak at 1025 to 1018 cm^{-1} (fig. 2), as also observed by Sachtler et al. [6], indicates that the short V=O bonds in the V_2O_5/SnO_2 catalysts are weaker than those in pure V_2O_5. The weakening of the V=O bond can be a consequence of the incorporation of the Sn in the lattice of V_2O_5 or its reduced form during the melting process (fig. 2, v) as explained by Andersson [5].

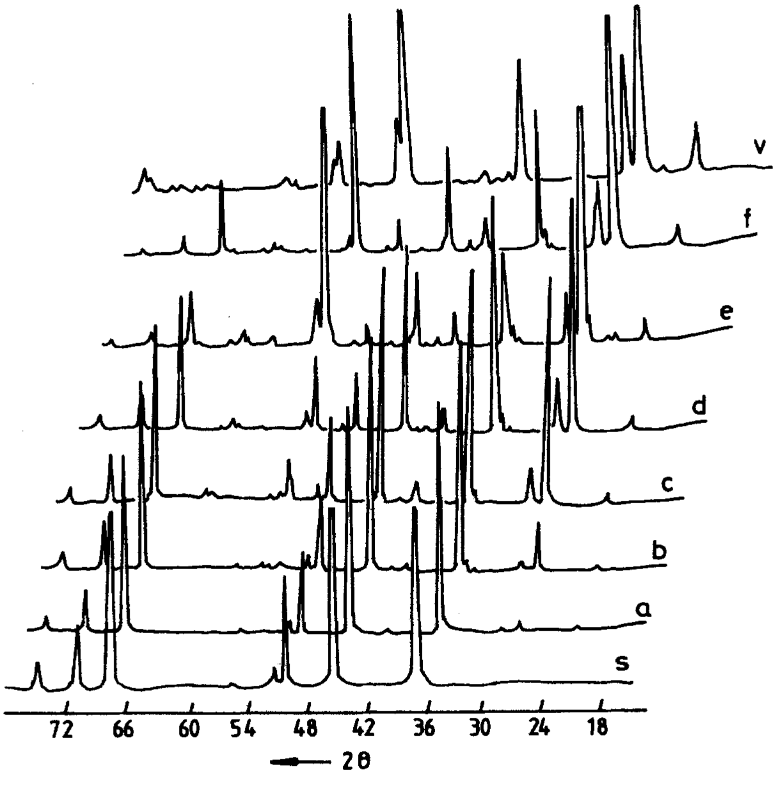

Fig. 1. X-ray diffraction patterns of unused catalysts with different vanadium contents (at%); (a) 20; (b) 33; (c) 50; (d) 57; (e) 67; (f) 70; (s) SnO_2 and (v) V_2O_5.

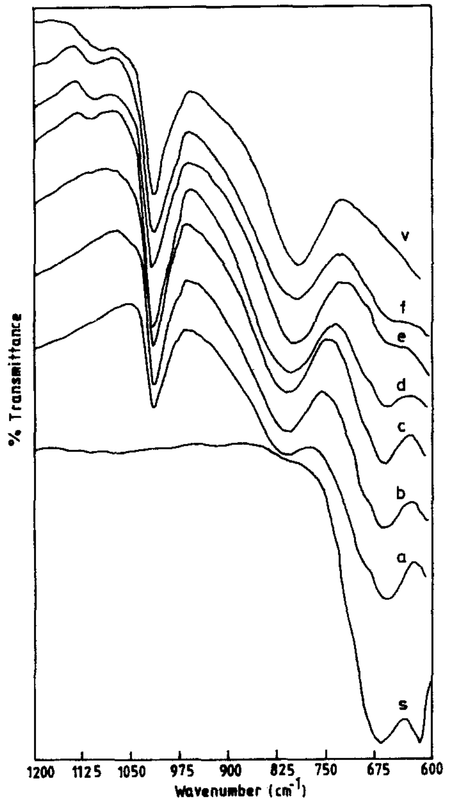

Fig. 2. FTIR spectra of unused catalysts with different vanadium contents (at%); (a) 20; (b) 33; (c) 50; (d) 57; (e) 67; (f) 70, (s) SnO_2 and (v) V_2O_5.

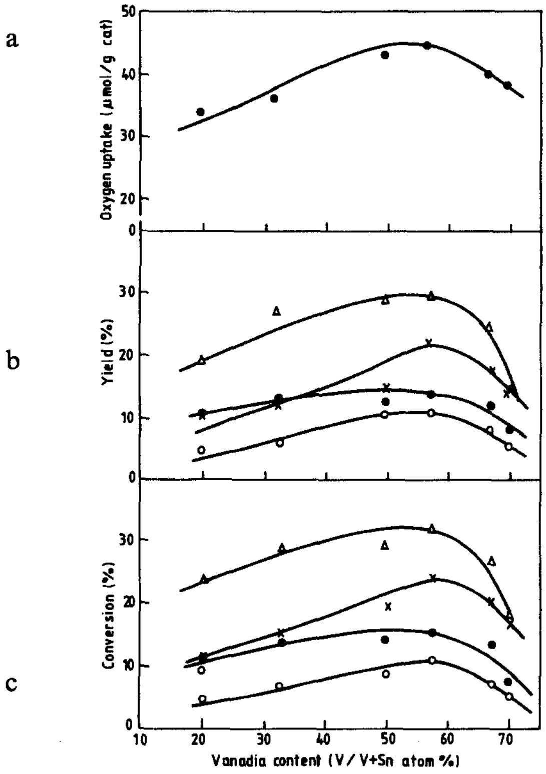

Fig. 3. Variation of (a) conversion of mesitylene, (b) yield of TCB and (c) oxygen uptake with the vanadium content of the catalysts; (○) 340°C; (●) 380°C; (×) 420°C; (△) 460°C.

Fig. 3 shows the changes in the conversion of mesitylene and the yield of TCB as a function of V content of the catalysts at different reaction temperatures. The conversion levels and the extent of the TCB yield have increased upto a vanadium concentration of 57 at% and then onwards they show a decreasing trend. A shift in the position of the most intense peak observed at 1018 cm^{-1} in the fresh catalysts to 998 cm^{-1} in the used catalysts (fig. 4) is an important observation from the FTIR spectra of the used catalysts. It is known that the reaction medium can reduce the vanadia to its lower oxidation states and the presence of lower oxides of vanadium has a great effect on both the activity and selectivity in the ammoxidation reactions [10,11]. Andersson [5] has stated that the coherent boundaries between V_2O_5 and V_6O_{13} (obtained by the reduction of V_2O_5 at 459°C) are especially selective in the ammoxidation of picolines. Increase in the yield of TCB with increase in V content upto 57 at%, as observed in fig. 3, can be ascribed to these partially reduced or the coordinatively unsaturated species of vanadium (IR absorption at 1000–995 cm^{-1} [12], as evidenced from fig. 4) which increase with increase in V content.

Many authors [7,12] have reported that, when a mixture of V_2O_5 and SnO_2 was melted at temperatures in the range 1250–1600°C, at least a part of V_2O_5 exists in the amorphous phase apart from crystalline V_2O_5. This amorphous vanadia, which exhibits a characteristic IR band at 960–980 cm^{-1} (as observed in the form of a shoulder in fig. 2), is spread over the solid solution and enables easy removal of lattice oxygen. It can be expected that with the increase in the vanadium content

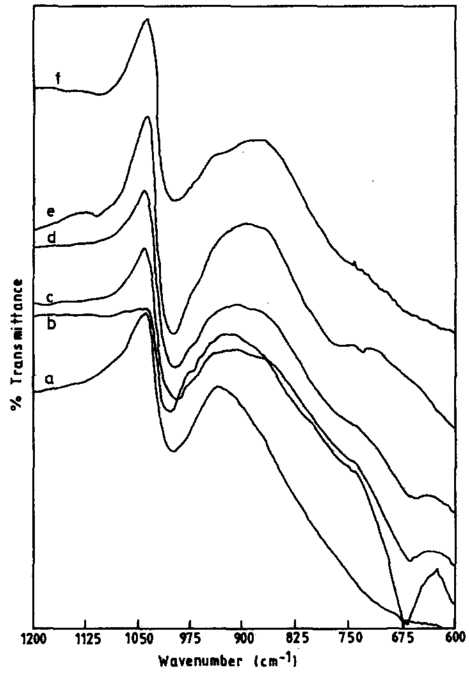

Fig. 4. FTIR spectra of used catalysts with different vanadium contents (at%); (a) 20; (b) 33; (c) 50; (d) 57; (e) 67; (f) 70.

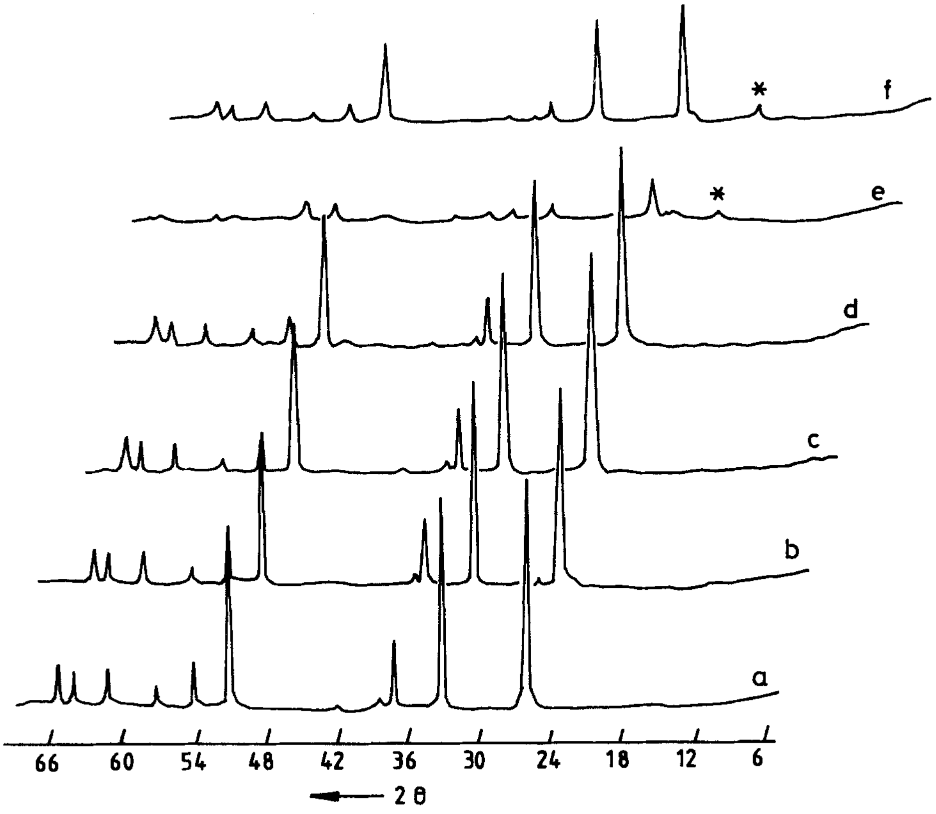

Fig. 5. X-ray diffraction patterns of used catalysts with different vanadium contents (at%); (a) 20; (b) 33; (c) 50; (d) 57; (e) 67; (f) 70.

this amorphous phase increases in quantity upto a definite level and a further increase of it in the catalyst leads to the formation of crystalline V_2O_5. Bordoni et al. [7] have proposed a model for the V–Sn–O system at increasing vanadia contents for samples prepared by solid state reaction. This model envisages formation of amorphous V oxide phase as discrete patches spread over the solid solution at lower V contents ($V<10\%$), their growth into a monolayer at compositions $10\%<V<30\%$ and finally formation of crystalline V_2O_5 at $V>30\%$. XRD patterns of the used catalysts with V content upto 57 at% (fig. 5) have exhibited the amorphous nature of vanadia. This observation is in contrast with the crystalline nature of V_2O_5 in the unused catalysts. However, catalysts with higher V content have revealed formation of crystalline V_2O_5. This observation is in accordance with the above hypothesis. Decrease in the activity as well as the TCB yield may be the result of the crystallinity imparted to the amorphous vanadia resulting into a reduced number of active sites. It is not possible to say, for sure, which phase of vanadia is active, but it may be expected that the catalyst is in an oxidation state between 4+ and 5+, as also thought of by Andersson and Jaras [4].

Chemisorption of oxygen is widely used as a potential technique in characterizing the coordinatively unsaturated sites (CUS) of vanadia. Many attempts have been made to titrate these CUS sites of reduced V_2O_5 species, particularly in alumina, silica and titania supported catalysts [13]. Oyama et al. [8] have suggested high temperature (640 K) chemisorption for a better estimation of the oxygen uptake. Fig. 3 also reveals that the oxygen uptake varies with the V content and exhibits a maximum at the same V content at which the activity of the catalyst is also maximum. The oxygen uptake values indicate that a V composition of 57 at% is the most favourable for the activity and the yield. Andersson and Jaras [4] and Andersson [5] have also used the same composition for their detailed characterization studies since the catalyst gave good results in the vapour phase oxidation of alkyl pyridines. It appears that beyond this composition the dispersion of the active species decreases due to the crystallinity of vanadia, which corroborates the XRD evidence given in fig. 5 and the model proposed by Bordoni et al. [7]. A good correlation obtained between the yield of TCB and the oxygen uptake (fig. 3) extends the applicability of HTOC to the fused V–Sn–O system as well. The V–Sn–O system, with a V content of 57% has given a good yield of TCB (30%). At lower reaction temperature (340°) the TCB selectivity is almost close to 100%.

4. Conclusions

It is concluded that better TCB yield could be obtained with the V–Sn–O system. At low reaction temperatures the selectivity is also maximum. It has been shown that HTOC could be extended to fused vanadium oxide catalysts to titrate the CUS sites.

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