Ammoxidation of toluene on MgF_2-supported monolayer vanadium oxide catalysts

J. Haber [1] and M. Wojciechowska [2]

[1] *Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland*
[2] *Institute of Chemistry, A. Mickiewicz University, Poznan, Poland*

Received 26 June 1991; accepted 1 July 1991

Tests show that V_2O_5/MgF_2 monolayers at 400 °C are active and selective catalysts, ammoxidizing toluene to benzonitrile with yields of more than 90%. IR spectra of toluene and NH_3 interacting at the surface show that, in the absence of NH_3, toluene is adsorbed in form of benzoate species. But in the presence of ammonia the spectra reveal mainly benzonitrile. A hypothesis is advanced that, on interaction of ammonia with the catalyst, NH^{2-} species substitute for oxide ions at its surface generating active sites for their nucleophilic insertion into the methyl group of toluene which has been activated by abstraction of hydrogen.

Keywords: Selective oxidation; selective ammoxidation; overlayer catalysts; benzonitrile; benzaldehyde; benzoic acid

1. Introduction

Oxidation and ammoxidation of toluene on vanadium oxide monolayer catalysts have recently been subjects of several studies [1–8]. Attempts to identify the reaction intermediates and elucidate the mechanism of the reaction have been undertaken using infrared spectroscopy [9,10]. These studies led to the conclusion that the reaction starts with the formation of the benzyl intermediate. In the absence of ammonia this intermediate interacts with surface lattice oxygen to form, consecutively, adsorbed benzaldehyde and benzoic acid precursors. These may be either desorbed or further oxidized to carbon oxides, or undergo degradation of the aromatic ring with the formation of maleic anhydride and carbon oxides. In the presence of ammonia, the benzyl intermediate reacts with adsorbed ammonia to give benzylamine, which is further oxidized via imine to nitrile. Comparison of the FT-IR evidence with the kinetic measurements of the ammoxidation of toluene seems to indicate [10] that selectivity is determined by the relative rates of the competitive reactions of the benzyl intermediate with surface oxygen and adsorbed ammonia. These results were obtained with V_2O_5/TiO_2 catalysts containing excess of V_2O_5 beyond that needed to complete the monolayer. The surface was thus populated by both nucleophilic and electrophilic oxygen and contained acid-base and redox centres which may have contributed to the complexity of the picture observed. It therefore seemed interesting to repeat the experiments using MgF_2 supported monolayer vanadium oxide catalysts, which contain oxygen only in the VO_x polyhedra, in the hope that additional information will be obtained concerning the mechanism of the reaction and the character of the intermediates involved.

2. Experimental

PREPARATION OF CATALYSTS

Samples of V_2O_5/MgF_2 catalysts were prepared by precipitation from the solution of ammonium metavanadate onto the suspension of freshly precipitated magnesium fluoride. Details of the experimental procedure were described in ref. [11]. By using solutions of ammonium metavanadate of different concentrations, preparations were obtained with V/Mg atomic ratios between 0.1 and 0.36. The samples are hereafter denoted by the symbols MFV_x, where x is equal to the atomic ratio V/Mg expressed as a per cent, e.g. the sample with a V/Mg atomic ratio equal to 0.05 is designated MFV_5. The surface area as determined by BET method from the adsorption isotherms of nitrogen at liquid nitrogen temperature ranged from 30 m^2/g for pure support MgF_2 to maximum 94 m^2/g for the preparation MFV_{10} and 75 m^2/g for the MFV_{36}. Results of structural studies of these catalysts by XRD, XPS, EPR and IR are described in ref. [12].

INFRARED SPECTRA

The IR spectra were recorded using a double-beam Perkin-Elmer Model 580 spectrometer. The samples were prepared in the form of self-supporting thin wafers, which were placed in a vacuum cell equipped with NaCl windows. The wafers were outgassed under a pressure of 10^{-3} Pa at 400 ° C for 5 h, several portions of oxygen being introduced successively during this period, cooled to room temperature and their IR spectra were registered. Then ammonia was introduced at 400 ° C for 0.5 h, the sample was cooled to room temperature, outgassed for 1′ and the spectrum was registered. The sample was again heated to 400 ° C, toluene introduced for 0.5 h, cooled to room temperature, outgassed for 1′ and the spectrum was then registered. In the second series of experiments carried out with a new sample, the sequence of the introduction of reactants was reversed, toluene being introduced first and ammonia second.

DETERMINATION OF THE CATALYTIC ACTIVITY

The catalytic properties in ammoxidation of toluene were determined by the pulse microreactor technique at 390 ° C. The microreactor was filled with 0.1 g of the catalyst sample and pulses of 0.4 μl of liquid toluene and 0.5 ml of gaseous ammonia were introduced into helium as a carrier gas flowing at the velocity of 40 $cm^3.min^{-1}$. Analysis of the products was carried out by on-line gas chromatography using a 1 m column with Carbowax 1000 at 140 ° C.

3. Results

Curve 1 in fig. 1 shows the yield of benzonitrile observed when pulses of toluene and ammonia were alternately passed over V_2O_5/MgF_2 catalysts of different composition. Pure MgF_2 was completely inactive in this reaction. It may be seen that on increasing the load of MgF_2 with vanadium oxide the yield of benzonitrile rises and at the V/Mg molar ratio of about 0.1 attains a plateau corresponding to the yield of benzonitrile of about 65%. The amount of benzonitrile formed was gradually decreasing with the number of pulses, but returned back to the initial value when the surface was reoxidized by pulses of air introduced after pulses of ammonia (curve 2 in fig. 1). This indicates that the decrease of the yield of benzonitrile in successive pulses of toluene and ammonia was due to the depletion of oxygen in the vanadium oxide monolayer. The activity of catalysts was considerably higher when pulses of oxygen were introduced alternately with pulses of toluene and ammonia (curve 3 in fig. 1) so that yield of about 90% of benzonitrile was attained for catalysts with V/Mg ratio higher than 0.1. Obviously pulses of oxygen regenerate the active sites of the catalysts more effectively than air. It should be noted that the activity of pure V_2O_5 was low.

Fig. 2 shows the IR-spectra of the MFV_6 catalyst registered after exposing it to the vapours of toluene at 400 ° C (spectrum B) and then after introduction of ammonia at the same temperature (spectrum C). In the spectrum obtained after contacting the sample with toluene vapours, strong unperturbed aromatic ring vibrations around 1600, 1500 and 1450 cm^{-1} are visible indicating that during the interaction of toluene with the surface of the catalyst the aromatic ring remains unaffected. Simultaneously two strong bands appear at about 1550 and 1410 cm^{-1}, which can be assigned to the asymmetric and symmetric vibration of the benzoate ion [9]. The fact that the band at 1500 cm^{-1} is very strong and sharp may be explained by assuming that it results from an overlap of the ring vibration and a band, which together with the band at 1410 cm^{-1} may be assigned to the asymmetric and symmetric vibration of a benzoate group [9]. No bands at 1428, 1362 and 1300 cm^{-1}, quoted [10] to appear as strong after adsorption of toluene at room temperature on vanadia/titania catalyst and

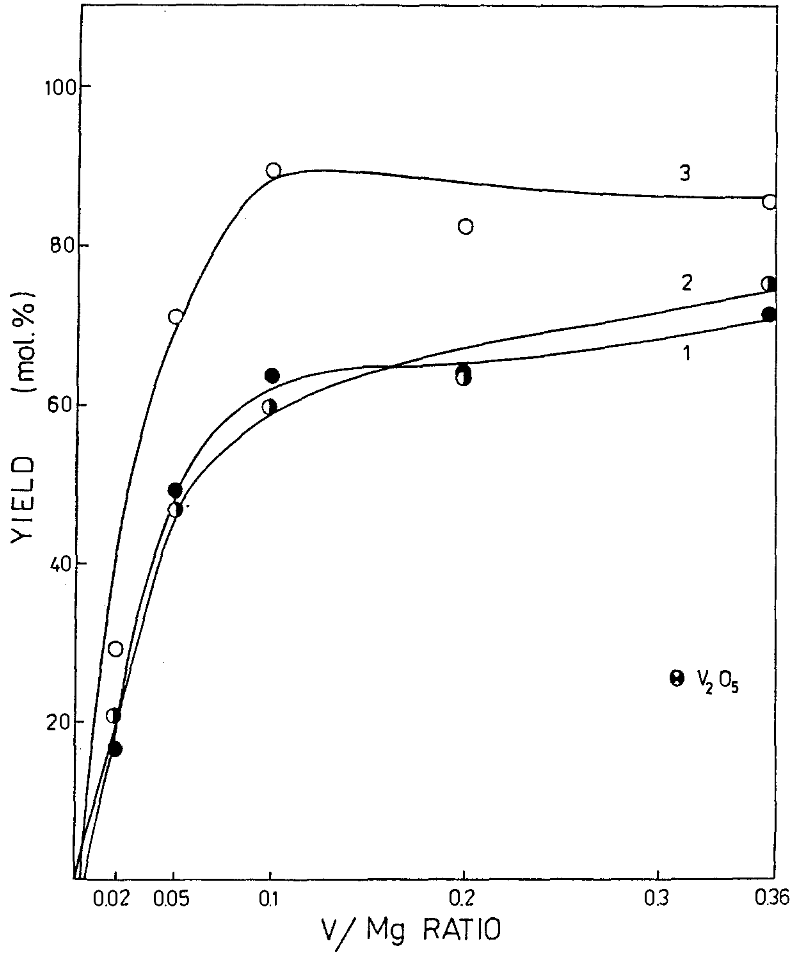


Fig. 1. Yield of benzonitrile in ammoxidation of toluene on V_2O_5/MgF_2 catalysts as function of the V/Mg atomic ratio.
1-pulses of toluene followed by pulses of ammonia.
2-after additional pulses of air.
3-oxygen.

interpreted as indicating the formation of adsorbed benzyl intermediate, could be detected in our spectra. This may be due to the fact that these bands disappeared after heating the sample to 250 °C and our spectra were obtained after exposing the sample to toluene vapours at 450 °C. Neither give our spectra any indication of the formation of the aldehyde-like intermediates, because no band could be discerned around 1700 cm^{-1}, due to the C=O stretching vibration and usually relatively intense.

After introduction of ammonia the band at 2240 cm^{-1} appears, which may be assigned to C≡N vibration, characteristic of benzonitrile, whereas the benzoate bands disappear completely and only the bands of aromatic ring at 1600 and

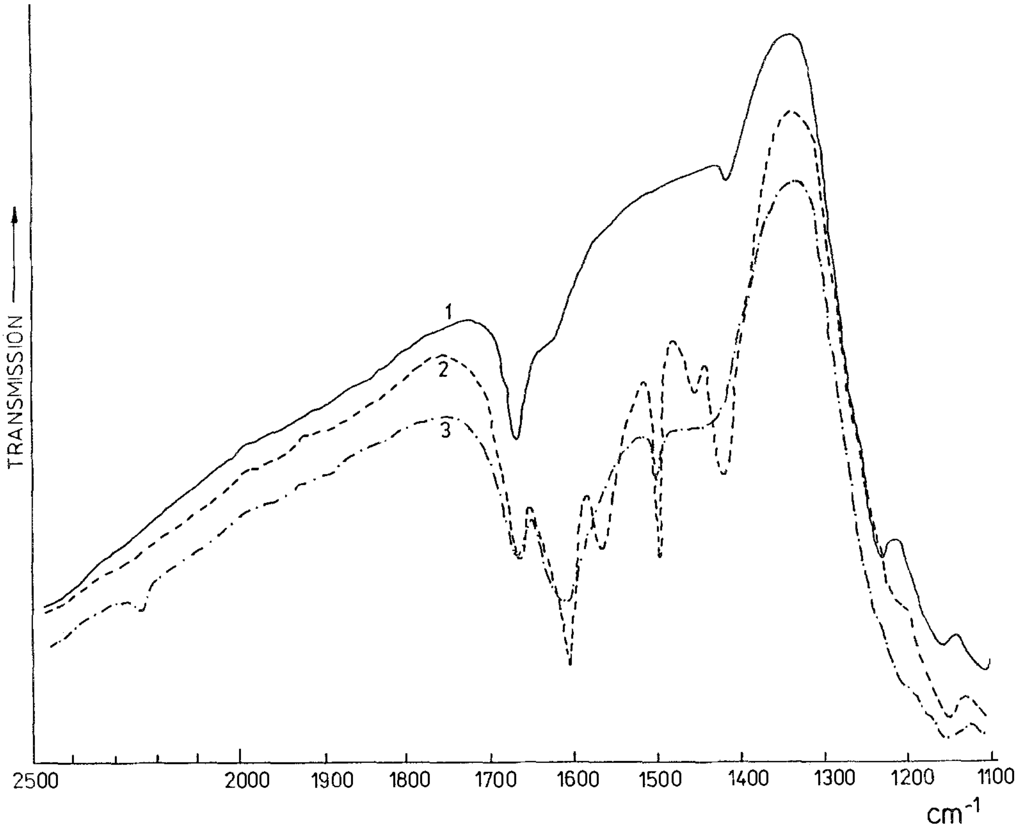


Fig. 2. IR spectra of MFV_5 catalyst after contacting at 400 °C with oxygen (curve 1) and then toluene (curve 2) and then ammonia (curve 3). Spectra registered at ambient temperature.

1500 cm^{-1} remain in the spectrum superimposed on the broad background band of ammonium ions at 1425 cm^{-1} and coordinatively bonded ammonia at 1610 cm^{-1}.

When the order of introduction of the adsorbates on the catalyst is reversed and ammonia is introduced first (fig. 3), two relatively broad bands appear: at 1425 cm^{-1} due to adsorbed NH_4^+ ions and 1610 cm^{-1} resulting from ammonia coordinatively bonded at Lewis acid sites. After introduction of toluene the C≡N band at 2240 cm^{-1} and the ring vibrations at 1600, 1500 and 1450 cm^{-1} appear indicative of the formation of benzonitrile, but no bands at 1550 or 1400 cm^{-1} which could indicate the formation of benzoate species.

4. Discussion

Our earlier investigations of the structure of MgF_2-supported vanadium oxide catalysts showed [12] that at low vanadium oxide loadings isolated VO_4 tetrahedra appear at the surface, which undergo polymerization to form chains of

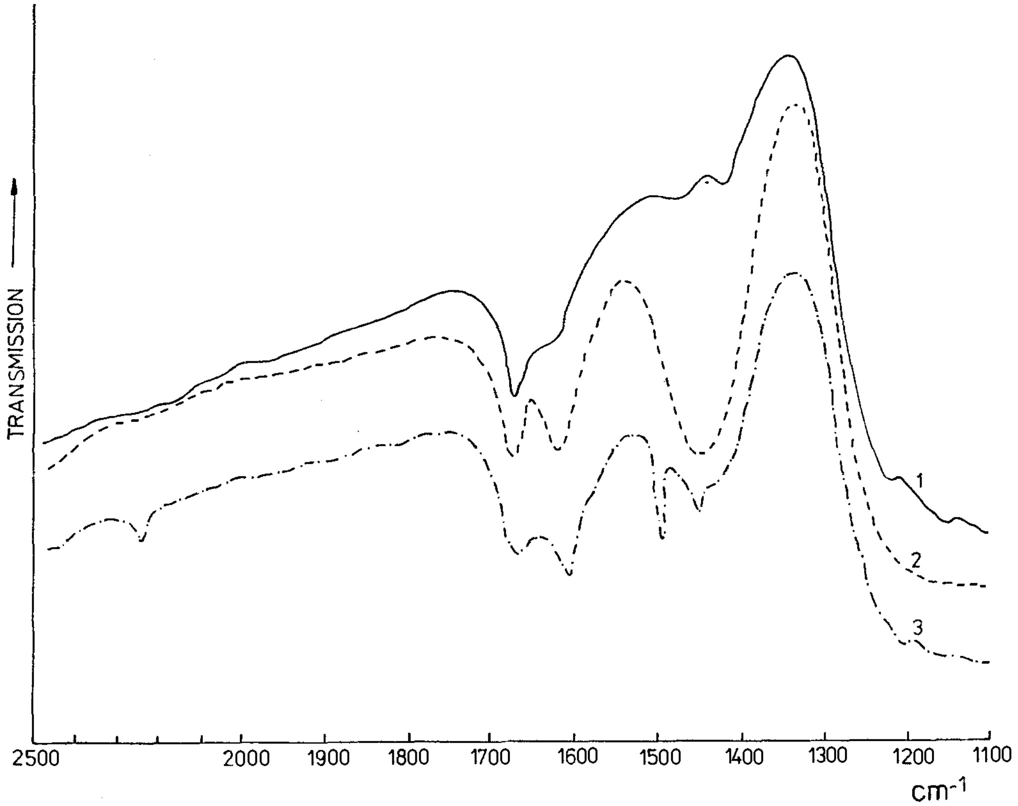
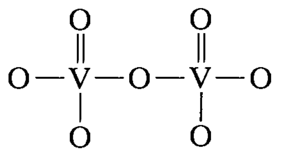


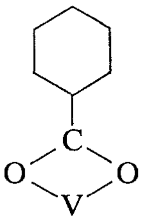
Fig. 3. IR spectra of MFV_5 catalyst after contacting at 400 °C with oxygen (curve 1) and then ammonia (curve 2) and then toluene (curve 3). Spectra registered at ambient temperature.

tetrahedra $(VO_3)_n$ of the metavanadate type or islands of trigonal pyramids. At higher concentrations polyvanadate species with octahedrally coordinated vanadium are deposited at the surface. Fig. 1 indicates that activity of the MFV catalysts increases with loading and attains a constant level beginning from the MFV_{10} catalyst for which the coverage with metavanadate attains saturation. Catalysts with higher loadings contain polyvanadate species. It may be thus concluded that monolayer islands of surface metavanadate species provide the active sites for ammoxidation of toluene. The characteristic structural elements of such monolayer are

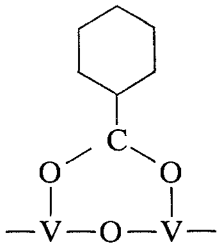


$$\begin{array}{ccccccc} & & \mathrm{O} & & \mathrm{O} & & \\ & & \| & & \| & & \\ \mathrm{O} & - & \mathrm{V} & -\mathrm{O}- & \mathrm{V} & - & \mathrm{O} \\ & & | & & | & & \\ & & \mathrm{O} & & \mathrm{O} & & \end{array}$$

with the bridging oxide ions playing the role of active sites [13] at which oxygen is inserted into the hydrocarbon molecule in the oxidation reaction. On interaction of such interface with toluene benzoate ions (I) and benzoate complexes (II):



(I)

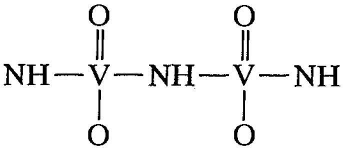


(II)

are formed as indicated by the IR-spectra (fig. 2b). They must be very reactive with ammonia, because on introduction of the latter they transform into benzonitrile. Important conclusions may be drawn from the observation that on the surface of the catalyst covered with ammonia no indication of the formation of benzoate species could be detected in the IR-spectra (fig. 3C). This would be difficult to explain if ammonia were present at the surface only in form of adsorbed species, because the interaction between adsorbed ammonia and gas phase toluene cannot be strong enough to provide an easy pathway for the reaction, and one would expect ammonia to be displaced by incoming toluene molecules, interacting strongly with surface oxide ions.

It is relevant to mention results of the studies of the behaviour of model MoO_3 catalysts with supported Bi^{3+} ions in oxidation and ammoxidation of propene [14]. Determination of the catalytic activity in pulse experiments, in which pulses of propene and ammonia were injected in different time intervals showed that the total conversion of propene remained constant, but the ratio of acrolein to acrylonitrile changed depending on the duration of the interval between the pulse of ammonia and that of propene. A hypothesis was advanced that on interaction with ammonia the oxide ions O^{2-} at the surface of the catalyst were exchanged by NH^{2-} groups, which performed the nucleophilic attack on the allyl species resulting in the formation of acrylonitrile. When the interval between pulses was longer, the surface NH^{2-} groups were oxidized by lattice oxygen of MoO_3, the surface becoming more and more populated with oxide ions and the proportion of acrolein formed being higher. This hypothesis was consistent with the observation that in this temperature range MoO_3 is rapidly reduced by ammonia.

A similar hypothesis may be advanced to explain the fact that no bands of benzoate species could be detected when toluene was introduced on the catalyst surface covered with ammonia. On interaction with ammonia the bridging oxide ions may be exchanged for NH^{2-} groups, forming surface structural units of the type



$$NH-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{V}}-NH-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{V}}-NH$$

which may play the role of active sites in the ammoxidation of toluene, the NH^{2-} group performing a nucleophilic attack on the methyl group of toluene in analogy with a nucleophilic attack on this group performed by oxide ion in the oxidation of toluene to bezaldehyde [13]. Although Busca et al. [10] were unable to find any IR evidence of the formation of amido- or imido surface species it should be borne in mind that, even at high coverage of the surface with these species, their total amount in the sample would be very small and their life time very short so that their detection in the IR region of structural vibrations of the oxide is very difficult.

References

[1] M. Niwa, H. Ando and Y. Murakami, J. Catal. 49 (1977) 92; 70 (1981) 1.
[2] A.J. van Hengstum, J.G. van Ommen, H. Bosch and P.J. Gellings, Appl. Catal. 8 (1983) 369.
[3] P. Cavalli, F. Cavani, I. Manenti and F. Trifiro, Catal. Today 1 (1987) 245.
[4] B. Grzybowska, M. Czerwenka and J. Sloczynski, Catal. Today 1 (1987) 157.
[5] M. Sanati and A. Andersson, Ind. Eng. Chem. Res. 30 (1991) 312.
[6] S.L.T. Andersson, J. Catal. 98 (1986) 138.
[7] Jingmin Zhu, B. Rebenstorff and S. Lars Andersson, J. Chem. Soc. Farad. Trans. I, 85 (1989) 3629; 3642.
[8] Jingmin Zhu and S.L. Andersson, Appl. Catal. 53 (1989) 251.
[9] A.J. van Hengstum, J. Pranger, S.M. van Hengstum-Nijhuis, J.G. van Ommen and P.J. Gellings, J. Catal. 101 (1986) 323.
[10] G. Busca, F. Cavani and F. Trifiro, J. Catal. 106 (1987) 471.
[11] J. Haber and M. Wojciechowska, J. Catal. 109 (1988) 23.
[12] J. Haber, J. Stoch and M. Wojciechowska, Surf. Interface Anal. 15 (1990) 711.
[13] J. Haber, in: *Structure and Reactivity of Surfaces*, eds. C. Morterra, A. Zecchina and G. Costa (Elsevier 1989) p. 447.
[14] K. Bruckman, J. Haber and T. Wiltowski, J. Catal. 106 (1987) 188.