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Selective Catalytic Oxidation of Acetonitrile

It has been discovered that acetonitrile can be selectively oxidized in the vapor phase to glycolonitrile (hydroxyacetonitrile) or, in the presence of water, to glycolamide (hydroxyacetamide) using vanadium oxide catalysts. Partial reduction of the catalysts is required to obtain optimum selectivities to the desired partial oxidation products. Crystalline V_6O_{13} present in active catalysts is apparently necessary for activation of acetonitrile by heterolytic C—H bond cleavage. A general mechanism for this new catalytic reaction is proposed. © 1986 Academic Press, Inc.

INTRODUCTION

Acetonitrile is a by-product of the catalytic ammoxidation of propylene and ammonia to acrylonitrile. Of the 240 to 320 million pounds of acetonitrile produced annually [based on worldwide production of acrylonitrile of 8 billion pounds per year and a 3 to 4 wt% acetonitrile by-product, see Ref. (*1*)], only a small amount is recovered for use as a solvent. The remainder is used as boiler fuel. Because of its relatively high chemical stability, acetonitrile has found limited application as a chemical intermediate. The paucity of reported acetonitrile reaction chemistry bespeaks the inherent difficulty in activating this molecule toward selective chemical transformations. However, recently it has been reported that acrylonitrile can be produced by the catalyzed reaction of acetonitrile with methane (*2*) or methanol (*3*).

It has now been discovered that acetonitrile can be selectively oxidized over select metal oxide catalysts to glycolonitrile (hydroxyacetonitrile); Reaction 1, or, in the presence of water, to glycolamide (hydroxyacetamide); Reaction 2.

$$CH_3CN + \tfrac{1}{2} O_2 \rightarrow HOCH_2CN \quad (1)$$

$$CH_3CN + \tfrac{1}{2} O_2 + H_2O \rightarrow HOCH_2C(O)NH_2 \quad (2)$$

The only existing chemistry for preparing glycolonitrile is by the stoichiometric reaction of HCN and formaldehyde. Glycolonitrile can be an intermediate in the manufacture of nitrilotriacetic acid (NTA), a general purpose chelating agent. In addition, recent work has shown that glycolonitrile also can be used as a starting material for the manufacture of the amino acid serine (*4*).

This report documents this newly discovered catalytic oxidation reaction and reports the results of our initial investigation into the nature of active catalysts. A general mechanism is presented that accounts for the observed reaction chemistry.

EXPERIMENTAL

Reactions were carried in the vapor phase at temperatures between 300 and 375°C in a fixed-bed microreactor (5 ml) with catalyst particles of 20 to 35 mesh and at atmospheric pressure. Contact times for the reaction ranged between 0.1 and 1.3 s. Condensible reaction products were collected in a water scrubber at ice-cold temperatures and analyzed by high-pressure liquid chromatography (HPLC). HCN was analyzed by titration with silver nitrate after addition of excess NaOH and NaI. Noncondensible reaction products were analyzed by gas chromatography.

Silica-supported vanadium oxide (80 wt% V_2O_5 + 20 wt% SiO_2) was prepared by coprecipitation by addition of ammonium-stabilized silica sol (Nalco 2327) to an aqueous solution of ammonium metavanadate (NH_4VO_3), evaporating to dryness, and

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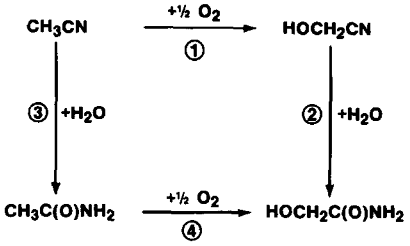
calcining in air up to 550°C. Surface area of the catalyst was 28 m^2/g.

Vanadium oxidation states in fresh and used catalyst samples were determined by permanganate titration after dissolution of the catalyst in phosphoric acid.

RESULTS AND DISCUSSION

Scheme 1 depicts the general reaction chemistry for selective catalytic oxidation/hydrolysis of acetonitrile. Glycolonitrile and glycolamide are the major reaction products in the scheme. The nonselective oxidation products, HCN, CO, and CO_2, result from C—C bond cleavage and oxidation of the hydrocarbon fragments. As the reaction network shows, glycolonitrile is the product of the direct oxidation of acetonitrile in the presence of oxygen. Glycolamide in turn results from the acid-catalyzed hydroloysis of glycolonitrile; independent experiments using glycolonitrile/water mixtures showed that 90 to 95% yields of glycolamide are obtained in the presence of active acetonitrile oxidation catalysts. Although hydrolysis of acetonitrile to acetamide can occur under acetonitrile reaction conditions, little glycolamide is produced when acetamide/oxygen mixtures contact active catalysts under typical acetonitrile reaction conditions. Thus reaction pathways 1 and 2 in Scheme 1 are the major routes from acetonitrile to glycolonitrile and glycolamide, respectively.



SCHEME 1. Selective reaction pathways for acetonitrile oxidation.

One of the most effective catalysts for the selective oxidation of acetonitrile to glycolonitrile or glycolamide is silica supported vanadium oxide (Table 1). It is noteworthy that the highest selectivity arises only after several hours on-stream. Figure 1 shows the X-ray diffractograms for both the fresh and used catalyst. Fresh catalyst exhibits diffraction peaks due only to V_2O_5 while diffraction peaks for both V_2O_5 and V_6O_{13} are clearly evident in the used catalyst. Reduction of V_2O_5 to V_6O_{13} clearly occurs during on stream operation. In fact, good activity and selectivity were observed only after reduction of some V_2O_5 to V_6O_{13}. An average vanadium oxidation state of about 4.6 is apparently necessary for optimum activity and selectivity. This corresponds to about a 40%/60% mixture of V_2O_5 and V_6O_{13} in the active catalyst. These results are consistent with previous studies of vanadium oxide catalysts for selective oxidation of *o*-xylene to phthalic anhydride (*5*) and selective ammoxidation of alkyl pyridines to cyanopyridines (*6*). Based on

TABLE 1

Catalytic Activity of Silica-Supported Vanadium Oxide Catalyst for Selective Oxidation of Acetonitrile

Reaction temp. (°C)	Contact time (s)	Feed $CH_3CN/O_2/N_2/H_2O$	CH_3CN conv.	Yield (%)		Selectivity (%)	
				G.N.	G.A.	G.N.	G.A.
300	1.3	1/0.6/11.4/0	26.4	6.8	—	25.6	—
350	0.15	1/0.6/11.4/1.3	4.5	—	2.9	—	63
350	0.15	1/0.6/11.4/2.4	5.0	—	3.7	—	73
375	0.15	1/0.6/11.4/1.3	8.7	—	4.9	—	56
375	0.10	1/0.6/11.4/1.3	3.2	—	2.4	—	75

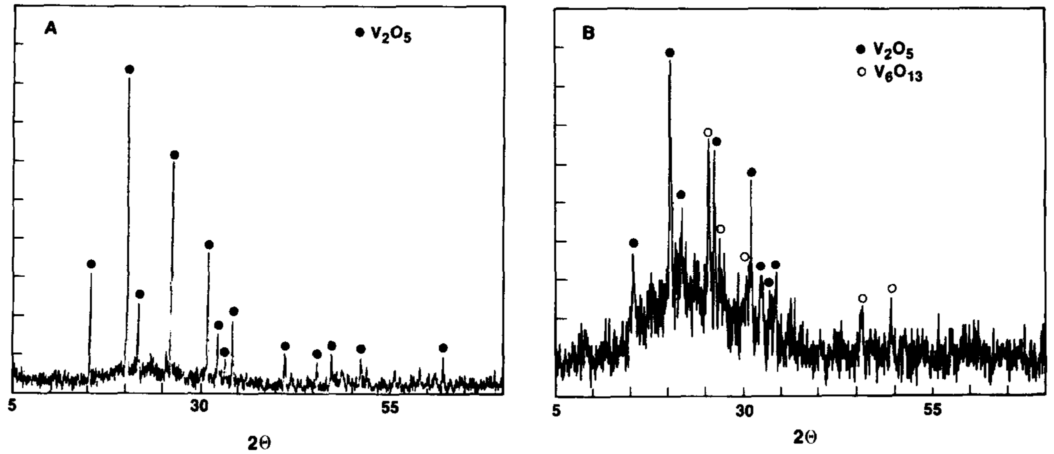
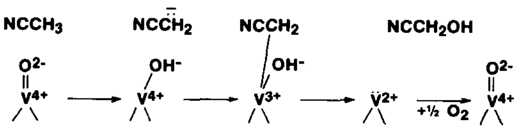


FIG. 1. X-Ray diffractograms of fresh and used vanadium oxide catalyst supported on SiO_2: (A) fresh catalyst, (B) catalyst after acetonitrile oxidation run.

these findings it can be inferred that surface centers containing V^{4+} are the active sites for acetonitrile oxidation.

The rate-determining step for selective hydrocarbon oxidation over vanadium oxide catalysts is generally hydrogen abstraction by a nucleophilic O^{2-} surface lattice oxygen (*7*). Because of the relatively high stability of the conjugate base of acetonitrile ($pK_a = 24$), this initial step in the reaction mechanism for acetonitrile oxidation is likely to be proton abstraction. A proposed mechanism for the selective oxidation of acetonitrile to glycolonitrile is shown in Scheme 2. Based on previous structural characterizations of V_6O_{13}/V_2O_5 selective oxidation catalysts (*8*), it is proposed that the active sites are the isolated $V^{4+}{=}O$ centers generated during reduction of V_2O_5. These defect centers most probably arise as a consequence of the growth of the V_6O_{13} from the V_2O_5 host structure. These centers are thus likely to be situated at the structural interface between the two phases, most probably at coordinately unsaturated sites at structural dislocations in the phase boundaries (*9*). Prior coordination of the acetonitrile molecule through the nitrogen lone pair may also occur and thereby facilitate proton abstraction.

Following proton abstraction, it is proposed that electron transfer from the acetonitrile anion to the electropositive vanadium cation center occurs followed by reaction of the methylcyano intermediate with surface hydroxyl. The reduced catalyst is reoxidized by oxygen from the vapor phase. The resulting glycolonitrile can then be hydrolyzed to glycolamide in the presence of added water on the acidic surface sites of vanadium oxide.



SCHEME 2. Proposed general mechanism for the selective oxidation of acetonitrile over vanadium oxide catalysts.

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