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Formation of Acetonitrile from Triethylamine on Oxide Catalysts

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Acetonitrile was found to be formed from triethylamine over ZrO_2 by TPD and IR experiments. The activity was higher than that of a strongly acidic SiO_2-Al_2O_3. No acetonitrile was formed over a strongly basic MgO.

It has been reported that a weakly acidic and weakly basic zirconium oxide shows specific catalytic activities for the cleavage of C-H bond1) and the hydrogenation of 1,3-butadiene by a molecular hydrogen and by hydrogen donor molecules such as cyclohexadiene,2-4) and high selectivities for the formation of α-olefin from sec-alcohol5) and the synthesis of isobutane from CO + H_2.6) The surface properties have been investigated by IR spectroscopy.7) These characteristic behavior of ZrO_2 is considered due to the acid-base bifunctional catalysis, since the catalysis by cooperation of a weak acid with a weak base is known to be superior sometimes to the catalysis by a simply strong acid or base.8,9) In the present work acetonitrile (AN) has been found, for the first time, to be formed from triethylamine (TEA) at relatively moderate temperature over ZrO_2.

Zirconium oxide was prepared by hydrolysis of zirconium oxynitrate, $ZrO(NO_3)_2$, with aqueous ammonia (28%), followed by drying the washed precipitates at 393 K and calcining in air at 873 K for 24 h. Silica-alumina was N 631 (L) SiO_2-Al_2O_3 of Nikki Co. Ltd., which was calcined at 773 K for 5 h. Magnesium oxide was MgO of Merck Co. Ltd., which was evacuated at 1073 K for 2 h. The surface areas of ZrO_2, SiO_2-Al_2O_3, and MgO were 30, 396, and 93 $m^2\ g^{-1}$, respectively, by the BET method. Triethylamine obtained from Wako Pure Chem. Ind. Ltd. was purified by repeated freeze-thaw cycles and a trap-to-trap distillation by passing through KOH and molecular sieves 3A.

Prior to the temperature programmed desorption (TPD) experiments, ZrO_2 and SiO_2-Al_2O_3 were pretreated by the following steps to remove completely any carbonaceous contaminants. A typical procedure for ZrO_2 was as follows. A 100 mg of sample was first oxidized in situ under 2.67 kPa of oxygen at 873 K for 1 h after 3 h of evacuation at the same temperature. After 20 min evacuation of the oxidized sample at 873 K, another 2.67 kPa of oxygen was admitted and then the sample was cooled down to room temperature in the oxygen atmosphere. In case of SiO_2-Al_2O_3, evacuation and oxidation temperatures were 773 K.

TPD experiments were carried out as follows. A sample was exposed to 1.33 kPa of TEA for 30 min after 1 h of evacuation at room temperature, followed by outgassing for 1 h and then the TPD procedure was started. The temperature was increased linearly at the rate of 10 K min^{-1}. The desorbed gases were analyzed by a NEVA NAG-515 mass spectrometer at an ionization voltage of 90 eV. Peak intensities of desorbed gases were normalized by using Ar (ca. 0.1 Pa) as an internal standard, which was constantly leaked into the system. On-line data treatment was supported by a NEC PC9801 personal computer.

IR spectra of self-supported discs were recorded on a JASCO 701-G infrared spectrometer.

Figures 1 and 2 show the TPD profiles of the fragments at m/e=58 and 28, and m/e=41, respectively, of TEA desorbed from the surfaces of ZrO_2, SiO_2-Al_2O_3, and MgO. Fragment pattern analyses revealed that the fragments at m/e=58 and 41 were characteristic for TEA, AN, respectively. The fragment of m/e=28 came from TEA, AN, and ethylene.

A single peak of TEA was observed at 363 K over SiO_2-Al_2O_3 and MgO, while two peaks were found at 383 K and 463 K over ZrO_2. The integrated amount of TEA desorbed was in the order of SiO_2-Al_2O_3 > MgO > ZrO_2 in accordance with the order of their surface areas. Since MgO gave no other peak, TEA is the sole desorbed substance; no decomposition takes place. The peak of m/e=28 at 693 K on SiO_2-Al_2O_3 is mainly composed of ethylene, because the contribution of AN to the fragment of m/e=28 is only 10%. Thus TEA adsorbed on SiO_2-Al_2O_3 desorbs mainly as TEA itself and only a small fraction can decompose to yield AN and ethylene during the TPD process.

ZrO_2 gave a complicated TPD profiles, however, fragment pattern analyses indicate that the peak of m/e=28 at 523 K comes mainly from ethylene and the peak

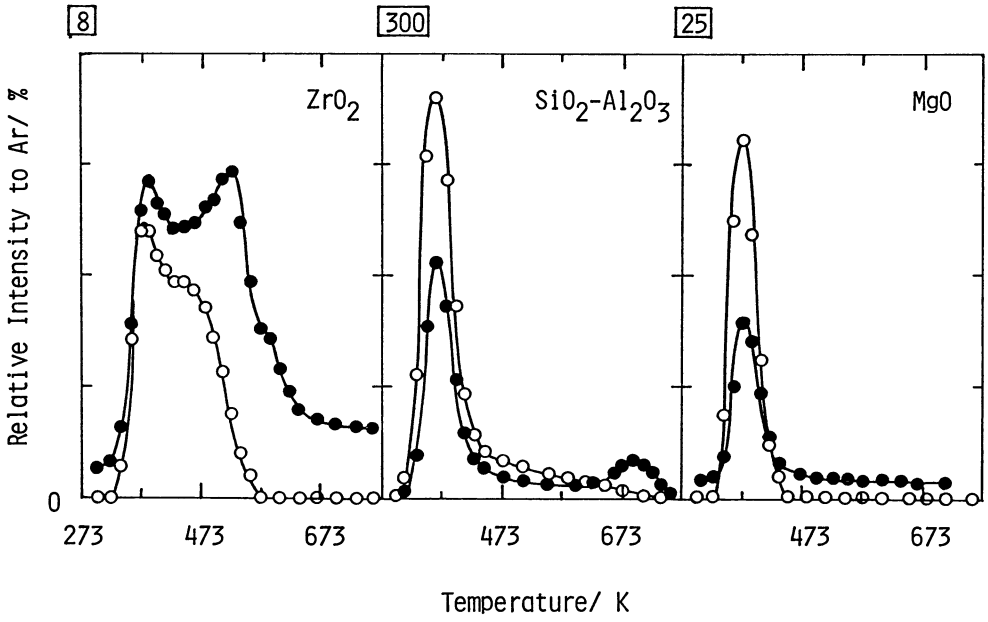
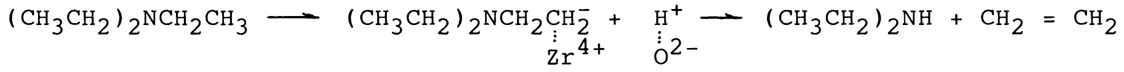


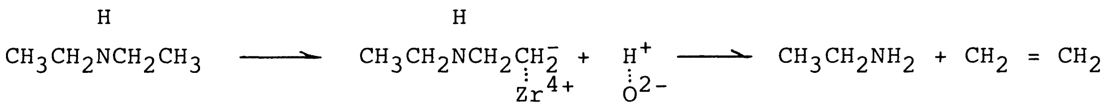
Fig.1. TPD profiles of triethylamine adsorbed on ZrO_2, SiO_2-Al_2O_3, and MgO. [-●-]:m/e=28, [-○-]:m/e=58. Values in ☐ indicate the scales of ordinates.

of m/e=41 at 593 K is AN. A part of the component of m/e=28 at 383 K may involve a fragment from TEA, but an accurate analysis was difficult because of a relatively higher background of m/e=28 (probably CO). So the production of ethylene at this temperatures on ZrO_2 is left to further investigations. It is noteworthy to mention that a significant fraction of TEA adsorbed on ZrO_2 decomposed to ethylene and AN.

Satoh et al. reported that ZrO_2 showed the highest activity among various metal oxides for the formation of 1-butene from butanamine,[10)] though no formation of nitrile was detected. They proposed a carbanion mechanism where the reaction is initiated by an abstraction of a H^+ from β-carbon by the basic site to form a carbanion which is stabilized by the acid sites. The formation of ethylene in the present work is tentatively interpreted by a similar mechanism as shown below.



$$(CH_3CH_2)_2NCH_2CH_3 \longrightarrow (CH_3CH_2)_2NCH_2\underset{\underset{Zr^{4+}}{\vdots}}{CH_2^-} + \underset{\underset{O^{2-}}{\vdots}}{H^+} \longrightarrow (CH_3CH_2)_2NH + CH_2 = CH_2 \tag{1}$$



$$CH_3CH_2\overset{H}{N}CH_2CH_3 \longrightarrow CH_3CH_2\overset{H}{N}CH_2\underset{\underset{Zr^{4+}}{\vdots}}{CH_2^-} + \underset{\underset{O^{2-}}{\vdots}}{H^+} \longrightarrow CH_3CH_2NH_2 + CH_2 = CH_2 \tag{2}$$

The formation of $(CH_3CH_2)_2NH$ and $CH_3CH_2NH_2$ was uncertain by the mass spectrometric analysis. Thus, they may remain on the surface as a form of $(CH_3CH_2)_2N^-$-Zr^{4+} or $(CH_3CH_2N)^=$-$(Zr^{4+})_2$, until they decompose to give ethylene and AN.

TPD profiles of AN from TEA adsorbed on ZrO_2 and SiO_2-Al_2O_3 are compared in Fig. 2. The peaks appeared at 593 K over ZrO_2 and at 693 K over SiO_2-Al_2O_3. TPD study of neat AN over ZrO_2 and SiO_2-Al_2O_3 revealed that the desorption peak temperatures were lower than that of AN formed from TEA. This suggests that AN formed from TEA at such high temperatures was immediately removed from the surface of ZrO_2 and SiO_2-Al_2O_3 and that the difference in peak temperature reflects the relative reactivity of the decomposition

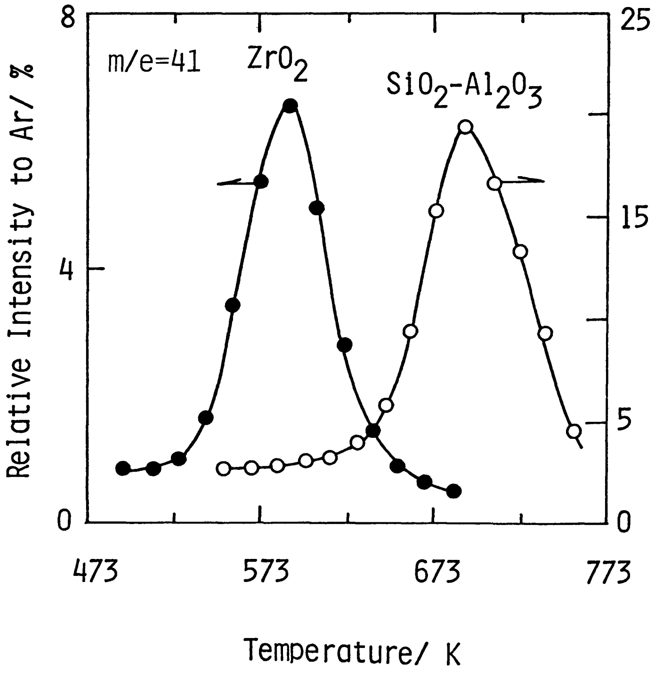


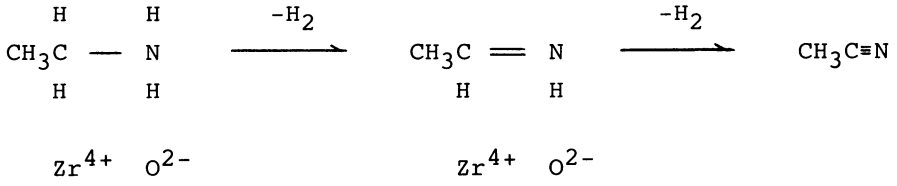
Fig.2. Formation of acetonitrile in the TPD process of triethylamine adsorbed on ZrO_2(–●–) and SiO_2-Al_2O_3(–○–).

reaction of TEA adsorbed to AN over ZrO_2 and SiO_2-Al_2O_3. Since the peak temperature of AN was lower over ZrO_2 than over SiO_2-Al_2O_3, it can be concluded that ZrO_2 is more active than SiO_2-Al_2O_3 for the formation of AN. MgO is completely inactive for this reaction.

From a comparison of the relative integrated intensities of TEA and AN on ZrO_2 and SiO_2-Al_2O_3, it is clear that much more portion of TEA was converted to AN over ZrO_2 than over SiO_2-Al_2O_3.

The formation of AN on ZrO_2 was also supported by the observation of the appearance of characteristic IR bands (near 2180 and 2320 cm^{-1}) of C≡N stretching frequencies when TEA was contacted to ZrO_2 below 623 K on the one hand, and by the gas chromatographic detection of AN during the reaction of TEA in a closed recirculation system at 593 K on the other.

Since a typical solid base, MgO, was inactive and a strong solid acid, SiO_2-Al_2O_3, showed lower activity for the formation of AN, the high activity of ZrO_2 could be interpreted in terms of the acid-base bifunctional catalysis as shown below.



A simultaneous evolution of hydrogen with AN was confirmed by the TPD experiments.

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