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Heterogeneous Liquid Phase Oxidation of Alcohols with Zirconia-Supported Vanadium Oxide as Solid Oxidizing Reagent

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An oxidant in heterogeneous system was obtained by impregnating $Zr(OH)_4$ with NH_4VO_3 followed by calcination in air at 500 °C; this material (V_2O_5/ZrO_2) converted alcohols into the corresponding aldehydes or ketones at moderate temperatures in solvent.

Jones (CrO_3-H_2SO_4-acetone), Collins (CrO_3-pyridine), and PCC (CrO_3-pyridine-HCl) reagents are well-known oxidation reagents and widely used in homogeneous liquid system.[1)] As for heterogeneously used reagents, supported vanadium oxides on silica, titania, alumina, and zirconia are used in gas-phase reaction.[2-5)] However good insoluble reagents for liquid-phase oxidation are quite few and highly desirable. Replacement of homogeneous reagents by insoluble solids simplifies with their separation from the reaction mixture as well as regeneration and reutilization of the reagents.

We reported that solid superacids could be prepared by supporting SO_4, WO_3, and MoO_3 onto ZrO_2, SnO_2, TiO_2, and Fe_2O_3, and that these materials are good oxidation catalysts in gas-phase reactions.[6,7)] This method of reagent preparation was applied to oxidation chemicals, and we found that vanadium oxide supported on zirconia is a good reagent for heterogeneous liquid-phase oxidation of alcohols at moderate temperature.

First $Zr(OH)_4$ was prepared by hydrolysis of $ZrOCl_2$ or $ZrO(NO_3)_2$ with aqueous ammonia, following drying, and clashing the solid to particle below 100 mesh. This powder (6.46 g) was added into a solution of NH_4VO_3 (0.5 g) dissolved in 300 mL of 28% NH_4OH. Water was evaporated and the material was calcined at 500 °C in air for 3 h.[8)] The concentration of V_2O_5 was 10 wt% based on ZrO_2. Oxidation of alcohols was carried out with stirring a mixture of 50 mg of alcohols, 5.0 mL of solvent, and 0.3-0.5 g of the oxidant. The products separated from the solid were analyzed by gas chromatography with a 25 m capillary column of PEG-20M.

The liquid-phase oxidation of cyclohexanol to cyclohexanone was performed at reflux temperature of toluene, and the reactivity was found to be highly dependent on metal oxides used as supports. Table 1 shows the yields of cyclohexanone after 2 and 6 h with V_2O_5 supported on various metal oxides. The oxide used for a carrier were prepared from $Ti(OCH(CH_3)_2)_4$, $Fe(NO_3)_3$, $Al(OCH(CH_3)_2)_3$, and $Si(OC_2H_5)_4$ as starting materials in the same manner as ZrO_2. All the materials were calcined at 500 °C for 3 h in air.[8] Table 1 shows that ZrO_2 is the most effective support. Unsupported V_2O_5, prepared by calcination of NH_4VO_3 at 500 °C, showed no activity at all. It is clear that the oxide acts as oxidizing agent by interaction with the support ZrO_2. V_2O_5/TiO_2 also showed high activity, but particles of this material became too fine to remove from the reaction mixture by filtration.

Table 1. Effect of supports for the cyclohexanol oxidation to cyclohexanone [a)]

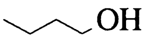
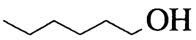
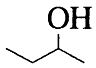
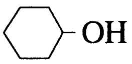
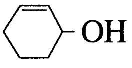
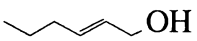
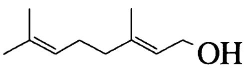
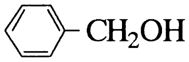
Supports of V_2O_5	Yield of cyclohexanone/%	
	2 h	6 h
ZrO_2	19	89
SiO_2	4	11
Al_2O_3	8	23
TiO_2	57	80
Fe_2O_3	9	14
none	0	0

a) Temperature; 110 °C, solvent; toluene.

The effect of concentration of vanadium oxide to ZrO_2 was also examined. The best activity was observed with 10 wt% of V_2O_5. Oxidation of various alcohols with V_2O_5/ZrO_2 was examined, and the results are shown in Table 2. Acyclic primary and secondary alcohols such as 1-butanol, 1-hexanol, and 2-butanol are only slowly oxidized to the corresponding aldehydes or ketones. However, benzyl alcohol is converted into aldehyde in good yield.

The V_2O_5/ZrO_2 oxidant was removed from the reaction, and the mixture was again heated, but it failed to react further. No vanadium was detected in the liquid phase. Therefore, the present reaction proceeds on the surface of the solid. The color of V_2O_5/ZrO_2 changes from pale yellow to gray after reduction of the vanadium from +5 oxidation state. And the measurement of temperature programmed reduction (TPR) also showed that vanadium is reduced from +5 to +2 and +3 oxidation state.9) After oxidation of cyclohexanol in toluene at 110 °C for 4 h, the V_2O_5/ZrO_2 oxidant was removed by filtration and then calcined at 500 °C in air for 3 h and then used for the same reaction. The color showed the oxidation state of vanadium to be returned to the initial state by recalcination in air. The yield of cyclohexanol in second run with recycled oxidation was 80% compared with 60% for the first reaction, thus the oxidation activity was remained or increased with repeated operation.

Table 2. Oxidation of Alcohols with V_2O_5/ZrO_2

Alcohol	Solvent	Temperature °C	Time h	Selectivity %	Yield[a] %
	CH_2Cl_2	40	6	100	48
	$(CH_2Cl)_2$	80	6	100	37
	CH_2Cl_2	40	5	100	37
	CH_2Cl_2	40	4	100	46
	Toluene	110	6	100	88
	Benzene	80	6	100	44
	Benzene	80	6	100	44
	CH_2Cl_2	40	6	100	54
	CH_2Cl_2	40	2	100	100

a) Determined by GC analysis.

References

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8) IR measurement of the catalysts showed that V_2O_5 was combined with the supports; unsupported V_2O_5 gave a band of 1020 cm^{-1} ($\upsilon V{=}O$), but the stretching band of V=O was not observed for V_2O_5 supported on ZrO_2, TiO_2, SiO_2, and Al_2O_3.
9) Oxidation of cyclohexanol(52 mg) with 240 mg of 9% V_2O_5/ZrO_2 in toluene at 110 °C for 7 h gave cyclohexanone in 44% yield. This yield is equivalent to the oxygen consumption of V_2O_5 reduced to V^{2+} and V^{3+} in the ration 28:72.

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