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Heterogeneous Liquid-Phase Oxidation of Alcohols with Solid Oxidizing Reagents of Vanadium(V) Oxide and Chromium(VI) Oxide Supported on Zirconium(IV) Oxide[1]

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The oxidizing reagents in a heterogeneous system were obtained by impregnating $Zr(OH)_4$ with NH_4VO_3 and $(NH_4)_2CrO_4$ followed by calcination in air at 773 K. These materials (V_2O_5/ZrO_2 and CrO_3/ZrO_2) converted alcohols into their corresponding aldehydes or ketones at moderate temperatures in a solvent with very high selectivity. Changes in the oxidation states of vanadium and chromium were investigated by a temperature-programmed reduction method (TPR). A linear relation was found between the yield of cyclohexanone formed from cyclohexanol and the amount of reduced vanadium or chromium, determined by TPR. It was confirmed that the active species of V(V) and Cr(VI) were reduced to V(II) and Cr(IV), respectively, in the oxidation process.

Jones (CrO_3–H_2SO_4–acetone), Collins (CrO_3–pyridine), and PCC (CrO_3–pyridine–HCl) reagents are well-known oxidation reagents and have been widely used in homogeneous liquid systems.[2] As for heterogeneously used reagents, supported vanadium(V) oxides on SiO_2, TiO_2, Al_2O_3, and ZrO_2 are used in gas-phase reactions.[3—6] However, good insoluble reagents for liquid-phase oxidation are very few and are thus highly desirable. The replacement of homogeneous reagents by insoluble solids simplifies their separation from the reaction mixture as well as regeneration and reutilization of the reagents.

We have 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.[1,7,8] This catalyst-preparation method was applied to oxidation chemicals. We found that vanadium(V) oxide and chromium(VI) oxide supported on zirconium(IV) oxide are good reagents for the heterogeneous liquid-phase oxidation of alcohols at moderate temperature. The oxidation numbers of vanadium and chromium varied from (V) to (II) for vanadium and from (VI) to (IV) for chromium during the oxidation process.

Experimental

Oxidizing Reagent Preparation. Zirconium(IV) hydroxide was obtained by hydrolyzing $ZrO(NO_3)_2 \cdot 2H_2O$ (Wako Pure Chemical) with aqueous ammonia, washing, drying at 373 K, and powdering the precipitate (100 mesh for oxidation and 32—60 mesh for TPR). The hydroxide (6.46 g) was impregnated with ammonium vanadate (NH_4VO_3, 0.5 g) in 300 mL of 28% aqueous ammonia, followed by evaporating water, drying, and calcining in air at 773 K for 3 h.[8] Impregnation of chromium(VI) oxide on the support was carried out in the same manner as described above using an aqueous solution of $(NH_4)_2CrO_4$. The concentrations of V_2O_5 and CrO_3 were 10 wt% based on the weight of ZrO_2 after calcination.

The oxides used for a support were prepared as follows. The hydroxides of $Si(OH)_4$, $Al(OH)_3$, and $Ti(OH)_4$ were obtained by hydrolyzing $Si(OC_2H_5)_4$, $Al[OCH(CH_3)_2]_3$, and $Ti[OCH(CH_3)_2]_4$ dissolved in dried ethanol with distilled water. The hydroxides were washed with water, filtrated, and dried at 373 K.

Aqueous ammonium was added to an aqueous solution of $Fe(NO_3)_3$ to precipitate $Fe(OH)_3$. The precipitate was washed with distilled water and dried at 373 K.

All of the materials were calcined at 773 K for 3 h in air after impregnation.

Reaction Procedures. The oxidation of alcohols was carried out while stirring a mixture of 50 mg of alcohols, 5.0 mL of solvent, and 0.3—0.5 g of the oxidation reagent. The oxidation reagent was suspended in the solvent and stirred for 30 min prior to the reaction. The products separated by filtration from the solid were analyzed by gas chromatography with a 25 m capillary column of PEG-20M. The yields shown in the Tables were calculated based on the peak areas of the product and the substrate.

TPR Measurement. The quantities of reduced vanadium of fresh and used reagents were estimated by the TPR method. A mixture of 50% H_2 in N_2 was used as a reductive gas. This mixture was purified by reduced copper to remove any trace oxygen, followed by passing through 3A molecular sieves to remove water. The total flow rate of the mixture was 40 $mL\,min^{-1}$. The change in the concentration of H_2 as a function of the temperature was monitored by a thermal-conductivity detector (TCD), yielding the TPR profile. Since water and organic compounds were evolved from used reagent held in the reactor, gas coming from the reactor was again purified by passing through silica gel and 3A molecular sieves before entering the TCD. The TPR was measured over the r.t.—773 K range at a temperature-programmed rate of 10 K min^{-1}.

Results and Discussion

The liquid-phase oxidation of cyclohexanol to cyclohexanone was performed over V_2O_5/ZrO_2 at the reflux temperature of toluene; the reactivity was found to be highly dependent on the 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. Table 1 shows that ZrO_2 is the most effective support. Unsupported V_2O_5, prepared by calcination of NH_4VO_3 at 773 K, showed no activity at all. IR measurements of the catalysts showed that V_2O_5 combined with the supports; although unsupported V_2O_5 gave a band at 1020 cm^{-1} (νV=O), the V=O stretching band was not observed for V_2O_5 supported on ZrO_2, TiO_2, SiO_2, and Al_2O_3. It is clear that the vanadium(V) oxide acts as an oxidizing reagent by interacting with the support ZrO_2. Though V_2O_5/TiO_2 also showed high activity, particles of this material became too fine to be removed from the mixture by filtration in the reaction process.

The effect of the concentration of vanadium(V) oxide to ZrO_2 was also examined. The highest activity was observed with 10 wt% of V_2O_5. The oxidation of various alcohols with V_2O_5/ZrO_2 and CrO_3/ZrO_2 was examined; the results are shown in Table 2. In all cases the oxidation proceeded with very high selectivity; no other products could be observed by a GLC analysis. Although acyclic primary and secondary alcohols, such as 1-butanol, 1-hexanol, and 2-butanol, are only slowly oxidized to the corresponding aldehydes or ketones, benzyl alcohol is converted into aldehyde in good yield.

After the V_2O_5/ZrO_2 oxidizing reagent was removed from the reaction mixture, even though the mixture was again heated, it failed to react further. Since no vanadium was detected in the liquid phase 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 the reduction of vanadium from the V(V) oxidation state. After oxidation of cyclohexanol in toluene at 383 K for 4 h, the V_2O_5/ZrO_2 oxidizing reagent was removed by filtration, calcined at 773 K in air for 3 h and then used for the same reaction. The color showed that the oxidation state of vanadium is returned to the initial state upon recalcination in air. Since the yield of cyclohexanol in the second run with recycled oxidation was 80% compared with 60% for the first reaction, the oxidation activity either remained or increased upon repeated operation.

Table 1. Effect of Supports for the Cyclohexanol Oxidation to Cyclohexanone[a)]

Support of V_2O_5	Yield of cyclohexanone/%[b)]	
	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; 373 K, solvent; toluene. b) Determined by GLC analysis.

The solid reagent of CrO_3/ZrO_2 showed a similar function regarding the oxidation of alcohols, and its activity was lower than that of V_2O_5/ZrO_2.

The TPR profiles of fresh and used reagents for cyclohexanol oxidation are shown in Fig. 1. The reduction of V(V) began at around 500 K, and attained its maximum at 650 K. The reduction was completed at 750 K. The area of the reduction peak, which means the relative amount of reduction, decreased along with increasing the yield of cyclohexanone. However, the temperature of the peak top didn't change in all of the samples. As is shown in Fig. 2, there was a linear relationship between the yield of cyclohexanone and the peak area of TPR profiles. The theoretical maximum yield of cyclohexanone obtained by extrapolating the linear line in Fig. 2 was 69%. Other theoretical maximum yields were calculated from the relation of the amounts of the substrate and reagent. The oxidation of cyclohexanol was carried out using 0.48 mmol of cyclohexanol and V_2O_5/ZrO_2 containing 0.2 mmol of vanadium ion. The theoretical maximum yield calculated based on the as-

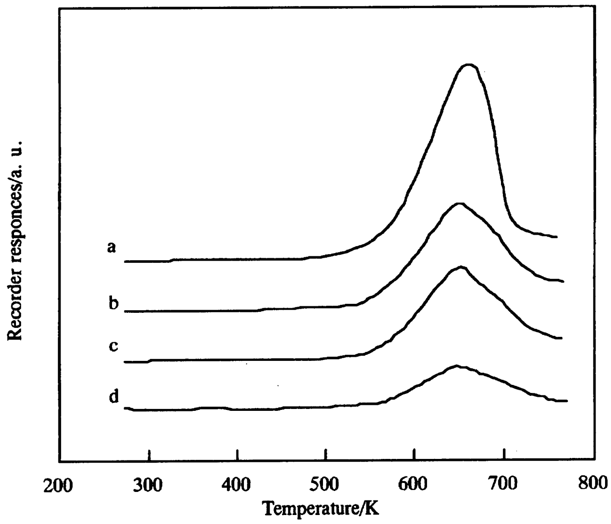

Fig. 1. Temperature-programmed reduction profiles of fresh (a) and used (b—d) V_2O_5/ZrO_2. Yield of cyclohexanone were 29.8 % (b), 30.7 % (c), and 51.6 % (d). Reaction conditions. Cyclohexanol: 0.48 mmol, V_2O_5/ZrO_2: 0.24 g (0.2 mmol as V(V)), Solvent: toluene 5 mL, Reaction temperature: 383 K. The mole ratio of V(V)/Cyclohexanol was 0.42.

Table 2. Oxidation of Alcohols with V_2O_5/ZrO_2 and CrO_3/ZrO_2

Alcohol	Reagent[a]	Solvent	Temp/K	Time/h	Yield/%[b]
1-Butanol	V	CH_2Cl_2	313	6	48
	Cr	CH_2Cl_2	313	6	12
1-Hexanol	V	$(CH_2Cl)_2$	353	6	37
	Cr	CH_2Cl_2	313	4	29
2-Butanol	V	CH_2Cl_2	313	5	37
	Cr	CH_2Cl_2	313	5	12
Cyclohexanol	V	CH_2Cl_2	313	4	46
	V	Toluene	383	6	89
	Cr	CH_2Cl_2	313	6	29
Cyclo-2-hexenol	V	Benzene	353	6	44
2-Hexen-1-ol	V	Benzene	353	6	44
Benzyl alcohol	V	CH_2Cl_2	313	2	100
Geraniol	V	CH_2Cl_2	313	6	54
	Cr	CH_2Cl_2	313	6	35
4-Phenyl-2-butanol	V	Toluene	383	48	45
	Cr	Toluene	383	48	17
5-Phenyl-2-pentanol	V	Toluene	383	48	48
	Cr	Toluene	383	48	17

a) V: V_2O_5/ZrO_2, Cr: CrO_3/ZrO_2. b) Determined by GLC analysis.

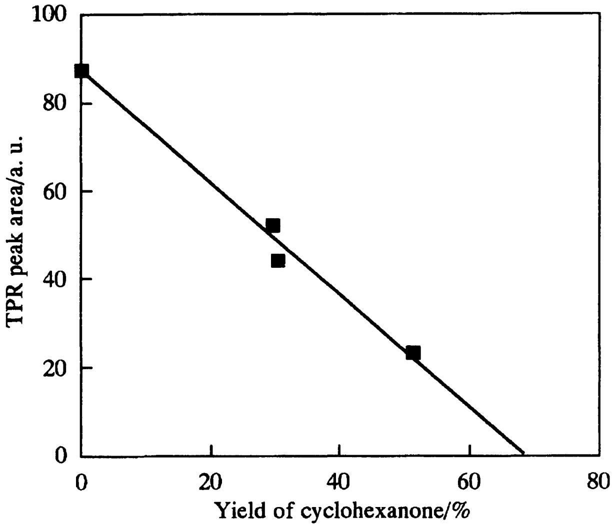

Fig. 2. Yield of cyclohexanone vs. TPR peak area of V_2O_5/ZrO_2.

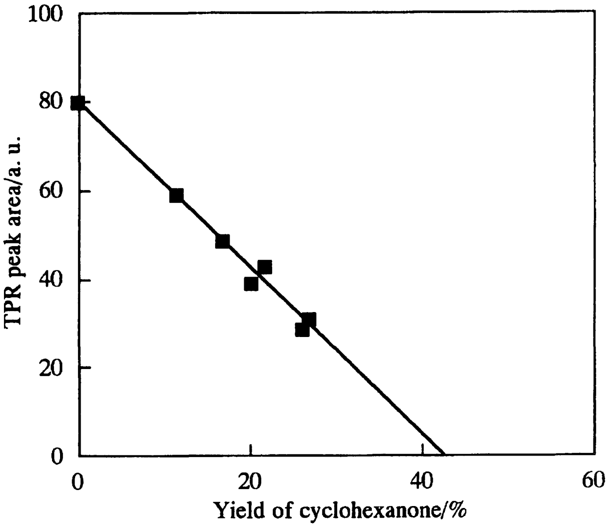

Fig. 3. Yield of cyclohexanone vs. TPR peak area of CrO_3/ZrO_2.

sumption that V(V) reduced to V(II) in the reaction was 62.5%. Those two values are close to one another.

H_2O evolved from a fresh sample during the TPR process was trapped on molecular sieves attached to the reactor. The total amount of H_2O, which was determined by changing the molecular sieves weight, corresponded to that of H_2O formed when V^{5+} reduced to $V^{2.5+}$ (on the average). Studies on gas-phase catalytic oxidation using vanadium oxides show that V(V) was reduced to V(III) in the presence of O_2.[9,10] In this study, a further reduction of the vanadium ion should proceed due to the absence of O_2.

The same analysis was performed on CrO_3/ZrO_2. As is shown in Fig. 3, a linear relationship between the yield of cyclohexanone and the peak area of TPR profiles can be observed. The theoretical maximum yield of cyclohexanone obtained by extrapolating the linear line was 42%. The theoretical maximum yield calculated from the relation of the amount of substrate and the reagent based on the assumption that Cr(VI) reduced to Cr(IV) in the reaction was 36%. It can therefore be concluded that Cr(VI) in the oxidizing reagent was reduced to Cr(IV) in the reaction process.

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