Gas-phase reduction of unsaturated ketones by hydrogen transfer reactions. A catalytic and spectroscopic study

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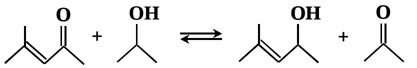
Introduction

Primary and secondary unsaturated alcohols are important organic intermediates for pharmaceutical, fragrance, polymer and food flavoring industries. Secondary unsaturated alcohols derived from allylic ketones are more difficult to obtain than the primary ones derived from unsaturated aldehydes because the substituent at the carbonyl hinders coordination of the C=O bond on the surface [1]. In addition, the hydrogenation of the C=C bond is kinetically and thermodynamically favored over that of the C=O group on noble metal catalysts [2]. Therefore, selective secondary allylic alcohol synthesis *via* allylic ketone hydrogenation on noble metals in gas or liquid phase is hardly achieved, irrespective of the H_2 pressure used.

The hydrogen transfer reduction (HTR) is an alternative to the conventional hydrogenation process for unsaturated ketone reduction. In the HTR reaction the reactant is contacted with a hydrogen source (usually an alcohol) on acid-base catalysts with no supply of molecular hydrogen, Scheme 1.



Scheme 1: HTR of mesityl oxide with 2-propanol

In this paper, we studied the gas-phase HTR of an α,β-unsaturated ketone, mesityl oxide, toward the allylic alcohol on acid-base catalysts. We discussed the effect of varying the operating conditions such as contact time, reactant ratio, hydrogen donor and reaction temperature on both the activity and product distribution. We also investigated the role played by the catalyst acid and base properties. By a combination of catalytic results and adsorption experiments by FTIR spectroscopy we identified reaction intermediates and analyzed stability of these species at different reaction conditions. Our goal was to elucidate the reaction pathways leading to allylic alcohol and saturated compounds and to ascertain the nature of the surface intermediates and surface active sites that promote these reactions.

Materials and Methods

MgO, Al_2O_3, ZrO_2, ZnO, Y_2O_3 and CeO_2 catalyst were prepared as previously described [3]. The total acid and base site densities were obtained from temperature-programmed desorption (TPD) of NH_3 and CO_2, respectively. FTIR experiments were carried out at room temperature in a Shimadzu FTIR-8101M spectrophotometer. Catalytic tests were conducted at 473-573 K and 100 kPa in a fixed bed reactor. A mixture of mesityl oxide (MO, 4-methyl, 3-penten-2-one) and typically 2-propanol (2P) was introduced *via* a syringe pump and vaporized in flowing N_2. Main products were the two unsaturated alcohol isomers (UOL_1, 4-methyl, 3-penten-2ol and UOL_2, 4-methyl, 4-penten-2ol), methyl isobutyl carbinol (MIBC), iso-mesityl oxide (i-MO), methyl isobutyl ketone (MIBK) and C_9 oxygenates.

Results and Discussion

FTIR of pyridine confirmed that the catalytic oxides present weak to moderate Lewis acidity but not measurable Brönsted acidity. Table 1 shows the catalyst acid and base properties as well as the selectivity to total UOL at 25 % MO conversion. Electronegative oxides such as ZrO_2 or Al_2O_3 tend to promote the C=C bond reduction giving the saturated ketone. On these oxides, 2-propanol decomposes into acetone and molecular hydrogen at high rates, which is detrimental to carbonyl reduction. Oxides combining weak Lewis acid cations and strongly basic oxygens such as MgO or Y_2O_3 are more selective toward allylic alcohols. Co-adsorption of both reactants on MgO monitored by FTIR show that 2-propanol and the C=O bond of mesityl oxide compete for the Mg^{2+} cations, probably forming a 6-atom cyclic intermediate that facilitates the C=O bond HTR in a Meerwein-Ponndorf-Verley mechanism. Catalytic experiments carried out on MgO show that the allylic alcohol yield (η_{UOL}) can be improved by increasing the contact time. Increasing the reaction temperature from 473 to 573 K, decreases the stability of reactions intermediates leading to MIBC at the expense of UOL formation, but the competitive double bond isomerization reaction toward i-MO is enhanced. Since MO conversion decreases but the UOL selectivity increases at high MO concentrations in the feed, an optimum η_{UOL} was measured for a MO/2P = 0.25 molar ratio. Finally, short-chain secondary alcohols are better hydrogen donors than the corresponding primary alcohols.

Table 1: Physicochemical Properties and Catalytic Performance

Catalyst	***S*$_g$** (m^2/g)	**Electronegativity** (Pauling unit)	**Base Site Density**[a] (μmol/m^2)	**Acid Site Density**[b] (μmol/m^2)	**Selectivity to UOL**[c] **(%)**
MgO	136	2.12	5.6	0.10	23.8
Y_2O_3	54	2.27	4.8	0.18	17.3
CeO_2	75	2.37	1.8	0.28	14.8
ZnO	18	2.38	<0.1	0.14	19.7
ZrO_2	83	2.51	0.3	0.27	15.9
Al_2O_3	300	2.54	0.1	0.37	9.1

[a] by TPD of CO_2 ; [b] by TPD of NH_3;
[c] 523 K, 100 kPa, N_2/2P/MO = 93.4/6.6/1.3, kPa, MO conversion = 25 %

Significance

The gas-phase C=O bond reduction of alkyl allyl ketones can be carried out by a hydrogen transfer process from a secondary alcohol without supplying gas-phase H_2. Selectivity is controlled by the catalyst electronegativity since the Lewis acid sites participate in the different possible reaction intermediates formed by coordination of the hydrogen donor alcohol and of the allyl akyl ketone through the C=O or C=C bonds. Selectivity can also be tuned by a proper choice of experimental conditions. Allylic alcohol yields of 44 % at 523 K can be obtained on basic catalysts such as MgO, a promising high value for a gas-phase reduction that contrasts with the usual values resulting from H_2-hydrogenation on noble metals.

References

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