Gas-phase hydrogen-transfer reduction of acrolein using 2-propanol over MgO/B_2O_3 and $SiO_2/AlPO_4$ catalysts

M.A. Aramendía, V. Borau, C. Jiménez, A. Marinas, J.M. Marinas, A. Porras and F.J. Urbano

Department of Organic Chemistry, University of Cordoba, Avda. San Alberto Magno s/n., E-14004 Cordoba, Spain
E-mail: qo1urnaf@uco.es

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Two MgO/B_2O_3 and $SiO_2/AlPO_4$ catalysts designated BM50 and PM2, respectively, were used in the gas-phase hydrogen transfer between acrolein and 2-propanol to obtain allyl alcohol and propanal. The acid–base properties and catalytic activity of the two systems were found to be rather different. Thus, the MgO/B_2O_3 catalyst is more selective towards allyl alcohol than is the $SiO_2/AlPO_4$ catalyst (conversion to the alcohol was 28% with the former and 0% with the latter). This special selectivity is discussed in terms of the different ways in which acrolein can be adsorbed on the catalytic surface as revealed by temperature-programmed desorption profiles and DRIFT spectra for pre-adsorbed acrolein.

Keywords: hydrogen transfer, acrolein, selectivity, MgO/B_2O_3, $SiO_2/AlPO_4$, adsorption

1. Introduction

The selective hydrogenation of α,β-unsaturated aldehydes is a well-documented reaction with important industrial applications [1]. Unsaturated alcohols make a major class of compounds for the chemical industry, particularly in the synthesis of fine chemicals. The catalytic hydrogenation of α,β-unsaturated carbonyl compounds to unsaturated alcohols is made difficult by kinetic and thermodynamic factors that lead to the preferential reduction of the olefinic double bound, so the yield in the unsaturated alcohol is usually low [2–5]. Much effort has been expended in developing ways to improve the selectivity towards the alcohol, especially by using efficient catalysts [6,7]. It is thus important to identify the variables that determine which of the double bonds in the starting compound is reduced. With catalytic reduction, the reactive bond is generally assumed to be the one involved in surface chemisorption. Controlling selectivity under these conditions thus essentially entails establishing the electronic factors that govern the way the α,β-unsaturated compound concerned is adsorbed on the catalytic surface used. So far, this is a scarcely explored subject [8].

In this work we studied the gas-phase catalytic reduction of acrolein, an α,β-unsaturated carbonyl compound, by hydrogen transfer from 2-propanol. We used two catalysts with differential acid–base properties, viz. a B_2O_3-doped MgO solid and a $SiO_2/AlPO_4$ mixed catalyst. Special emphasis was placed on the adsorption-controlled selectivity of the process.

2. Experimental

2.1. Catalyst synthesis

Catalyst MgO/B_2O_3, named BM50, was obtained by suspending 29.0 g of $Mg(OH)_2$ and 0.35 g of B_2O_3 in 200 ml of distilled water and sonicating the mixture for 1 h. The resulting solid was dried and air-calcined at 600°C for 4 h. The end product had an Mg/B ratio of 50 : 1. The $SiO_2/AlPO_4$ catalyst, named PM2, was synthesized from silica gel, $AlCl_3{\cdot}6H_2O$ and H_3PO_4 (85% by weight). The final composition of the solid was 80 : 20 w/w $SiO_2/AlPO_4$. A more detailed description of the synthetic procedures for both catalysts is given elsewhere [9,10].

2.2. Reactivity tests

Reactions were conducted on a 200 mm log×10 mm i.d. quartz reactor that was placed in a furnace the temperature of which was controlled to within ±1°C. The reactor output was fitted on-line to a VG Sensorlab mass spectrometer (Fisons Instruments, plc/VG quadrupoles) operated in the multiple ion monitoring (MIM) mode. In all experiments, we have monitored two peaks for each compound (the principal and other secundary for confirmation).

A fresh catalytic bed (typically 50 mg of catalyst) was used in each reaction. The carrier gas was nitrogen, used at a flow-rate of 120 ml/min. A mixture of 15% acrolein in 2-propanol (Aldrich Art. 17,598-7) was inserted into the reactor at a constant rate of 12 ml/min with the aid of a Braun perfusor. A temperature levelling time of 20 min was used. Data points were collected over a 150 min period. The absence of internal and external diffusion phenomena was experimentally checked. The absence of external diffusion was examined by analysing the way conversion changed as the different operating variables (sweeping and feeding flow-rates, and catalyst weight) were altered. We found our experimental conditions, described above, to lie in the kinetic control region. On the other hand, the absence of internal diffusion was confirmed by checking that conversion was independent of particle size.

Temperature-programmed surface reactions (TPSRs) were conducted in two temperature steps, viz. an isothermal period at 100°C for 30 min, followed by one in which the temperature was raised from 100 to 700°C at a constant rate of 10°C/min. The whole process was monitored via the mass spectrometer.

2.3. Temperature-programmed desorption and DRIFT experiments

In these experiments, both catalysts were cleaned up by passage of an Ar stream at 100°C at 50 ml/min for 30 min. The solids were then saturated with the probe molecule (pyridine, carbon dioxide or acrolein) at room temperature and subsequently flushed with a stream of pure Ar at 50 ml/min for 2 h in order to avoid physisorption.

Next, in TPD experiments, the temperature was raised at a constant rate of 10°C/min from room level to 600°C. Performing TPD experiments at a variable heating rate (from 6 to 12 K/min) allowed us to calculate the activation energies for desorption of the probe molecules, using the Kissinger equation [11]. The whole process was monitored via the mass spectrometer.

Alternatively, the catalyst containing pre-adsorbed acrolein was transferred to an Environmental Chamber from Spectra-Tech, and DRIFT recordings were obtained on a Bomen MB-100 instrument at 8 cm^{-1} intervals over the range 4000–400 cm^{-1} (an overall 256 scans). The procedure is described in greater detail elsewhere.

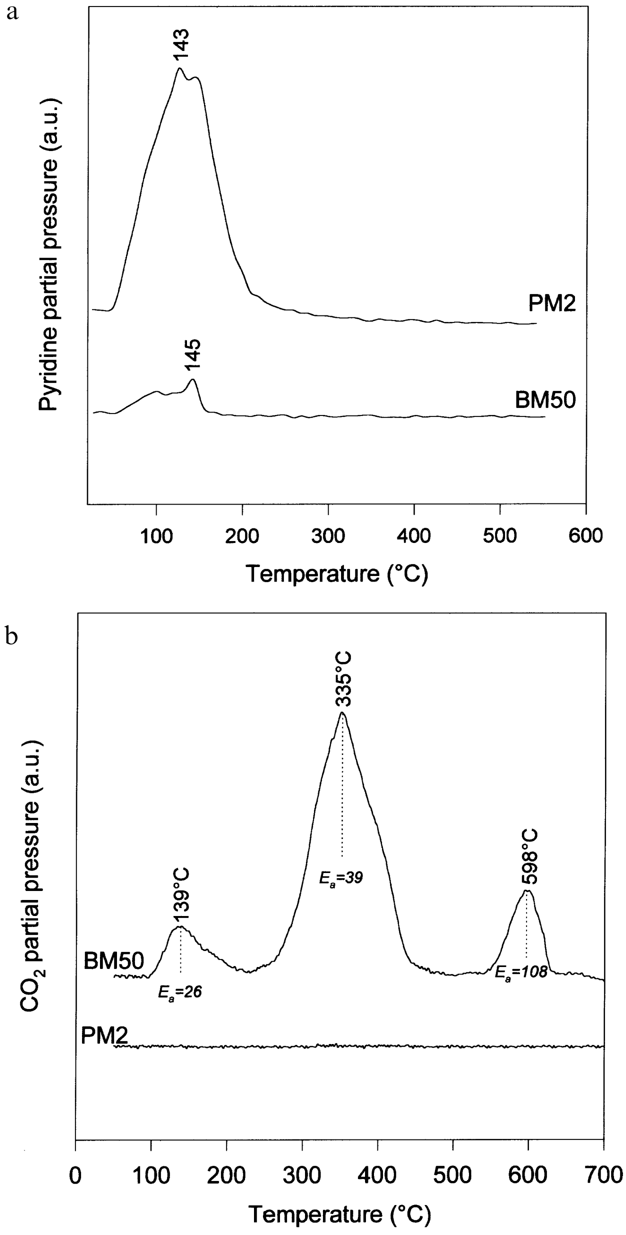

Figure 1. Temperature-programmed desorption profiles for pyridine (a) and carbon dioxide (b) adsorbed on the two solids studied. (E_a the activation energy of CO_2 desorption for each peak, in kJ mol^{-1}.)

3. Results and discussion

We analysed the effect of surface acid–base properties on the adsorption of acrolein, and hence on the selectivity towards allyl alcohol in the catalytic gas-phase hydrogen-transfer reduction of this α,β-unsaturated carbonyl compound by using two different catalysts, viz. MgO/B_2O_3 and $SiO_2/AlPO_4$, which were designated BM50 and PM2, respectively.

The surface acid–base properties of both solids were determined by temperature-programmed desorption of pyridine (acidity) and carbon dioxide (basicity) previously adsorbed on the catalysts [12,13]. Figure 1 shows selected TPD profiles and table 1 numerical data from these experiments. As can be seen from figure 1b, solid PM2 contains abundant acid sites but lacks basic properties. Conversely, solid BM50 is a strongly basic catalyst with three types of sites of variable basic strength as revealed by three peaks at 139, 335 and 598°C in the TPD profile. This catalyst also possesses a few acid sites from which pyridine is desorbed between about 50 and 150°C.

Figure 2 illustrates the temperature-programmed surface reaction between 2-propanol and acrolein monitored by mass spectrometry over the two catalytic systems studied. The profiles are highly revealing as regards activity and selectivity in the process. The hydro-

Table 1

Specific surface area (S_{BET}), acid–base properties (determined by temperature-programmed desorption of probe molecules), catalytic conversion (X, %) and selectivity towards allyl alcohol (S, %) of the catalysts studied

Catalyst	S_{BET} (m^2/g)	Acidity ($\mu mol_{PY}/g$)	Basicity ($\mu mol_{CO_2}/g$)	$T = 350°C$		$T = 400°C$		$T = 450°C$	
				X	S	X	S	X	S
PM2	402	115	–	5.8	0	7.2	0	10.5	0
BM50	104	28	440	13.1	25	24.1	28	37.7	31

gen transfer takes place over the temperature range 300–500°C. In previous work [10] on the same catalysts we found this range to coincide with that of 2-propanol dehydrogenation. Therefore, the hydrogen adsorbed on the catalyst only starts to reduce our α,β-unsaturated compound above 300°C. Solid BM50 is a more effective hydrogenating catalyst than is PM2 [10], so it results in greater overall conversion of acrolein (figure 2).

As regards selectivity in the reduction of acrolein, solid BM50 favours the formation of allyl alcohol, even in lower proportions than propanal, relative to catalyst PM2.

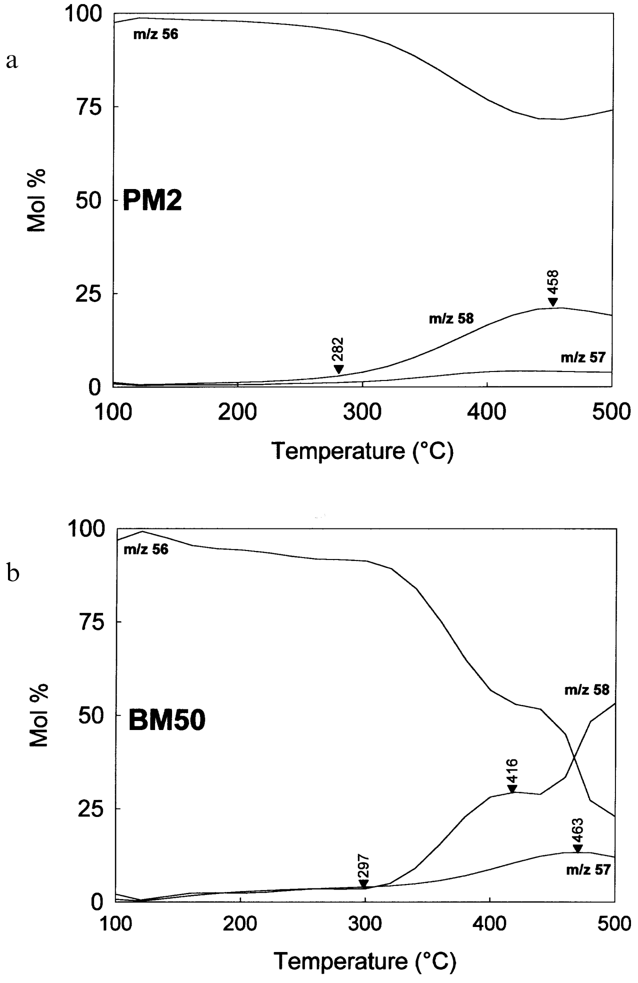

Figure 2. Temperature-programmed surface reaction profiles for the hydrogen-transfer reduction of acrolein from 2-propanol over catalysts PM2 (a) and BM50 (b) (m/z 56 acrolein, m/z 58 propanal, m/z 57 acrylic alcohol).

In the light of the results of the above-described temperature-programmed surface reactions, we carried out isothermal experiments over the previous temperature range in order to calculate both the specific activity and the selectivity of the reduction process. As can be seen from table 1, catalyst BM50 produced a much greater overall conversion than did solid PM2. As noted earlier, the hydrogen that effects the reduction comes from the dehydrogenation of 2-propanol on the catalyst surface. In this process, the hydrogenating power of the catalyst is reportedly proportional to the density of basic sites of the catalyst [14]. For this reason, solid BM50, with strongly basic surface properties, is a powerful dehydrogenating catalyst and thus favours the hydrogen-transfer reduction of acrolein.

More important, to our minds, are the selectivity results. Thus, solid PM2 exhibits 100% selectivity towards the aldehyde whereas solid BM50 is only 20–30% selective towards the unsaturated alcohol.

Provided a large enough amount of hydrogen from the dehydrogenation of 2-propanol is present in the medium, the selectivity of the process will ultimately be determined by acrolein adsorption. This in turn is controlled by the type of active sites predominating in the catalyst and by their relative strength. In order to obtain preliminary information on the adsorption of acrolein on both solids we performed temperature-programmed desorption experiments using acrolein adsorbed on both catalysts. The TPD profiles thus obtained are shown in figure 3. The graph reveals marked differences in the substrate adsorption on both types of solid. Thus, PM2 adsorbs acrolein on two different types of site (both at such low temperatures as 100 and 150°C); BM50 also exhibits two acrolein adsorption peaks, but at higher temperatures (194 and 227°C). Therefore, acrolein interacts rather differently with the two solids and is adsorbed to a different extent and with different strength on the two. In any case, solid BM50 appears to interact more strongly with acrolein than does PM2. The activation energies for the desorption of acrolein adsorbed on both catalysts, calculated from the Kissinger equation, confirm this assumption (E_a was 45 kJ mol^{-1} for acrolein adsorbed on BM50 and 31 kJ mol^{-1} for the probe adsorbed on PM2).

Delbecq and Sautet [8] hypothesized that an α,β-

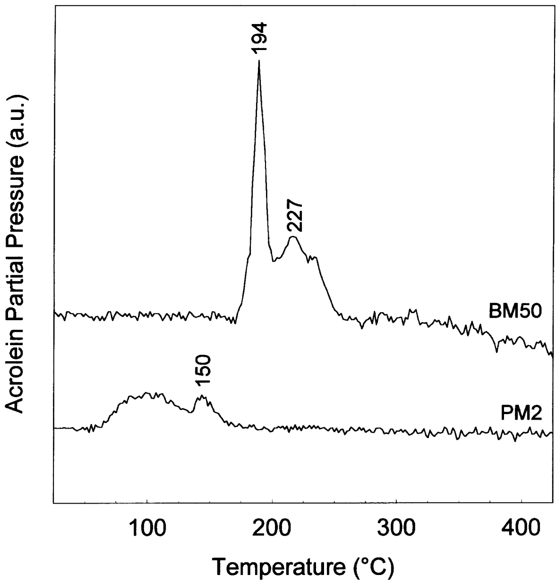

Figure 3. Temperature-programmed desorption profiles for acrolein on the two catalysts studied.

unsaturated carbonyl compound can be adsorbed in six different ways on a metal surface; their postulates can be extrapolated to solids with acid–base properties. Thus, species can be adsorbed via the C=C double bond, the C=O bond or both, to adopt a quasi-planar geometry.

In order to obtain further information on the process, we repeated the experiments at room temperature and performed a DRIFT study of adsorbed species. Once physisorbed acrolein was removed, the solids were transferred to a diffuse reflectance cell and their spectra recorded instead of performing the thermal desorption of the adsorbate. Figure 4 shows the DRIFT spectra for pure acrolein (a) and acrolein adsorbed on solids PM2 (b) and BM50 (c), recorded over the range 2000–1000 cm^{-1}. A comparison of the spectra in figures 1a and 1b reveals that adsorption on PM2 increases the frequency of the carbonyl bands for acrolein, which can be ascribed to decreased conjugation in the adsorbate. This, together with the disappearance of the typical bands of *R*–CH=CH$_2$ bonds (viz. –CH in-plane and out-of-plane bending, and –CH$_2$ in-plane bending) between 1300 and 1000 cm^{-1}, suggests that acrolein is adsorbed on solid PM2 via its C=C double bond. On the other hand, a comparison of the spectra in figures 1a and 1c reveals a markedly decreased carbonyl band and hence a decrease in the concentration of surface C=O groups. In addition, the frequency of the C=C stretching band increases from 1659 to 1667 cm^{-1}, which is suggestive of decreased conjugation. On the other hand, the bands in the 1300–1000 cm^{-1} region, typical of *R*–CH=CH$_2$, appear distinctly in the spectrum. These results suggest 1,2 C=C adsorption on solid PM2 and both this type of adsorption (which leads to a reduced C=C double bond) and 1,2 C=O adsorption (leading to a reduced carbonyl bond) on BM50. In any case, our data do not exclude 1,4 adsorption of acrolein on BM50, which would result in the reduction of the C=C double bond.

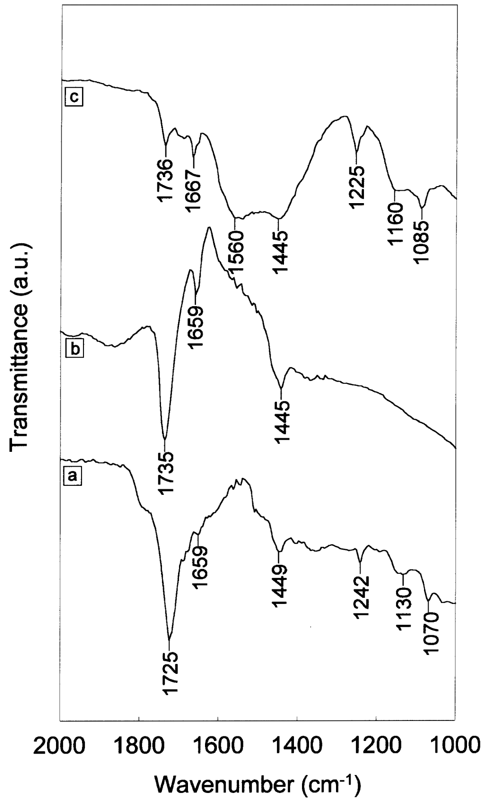

Figure 4. Diffuse reflectance IR Fourier transform (DRIFT) spectra for free acrolein (a) and acrolein adsorbed on catalysts PM2 (b) and BM50 (c).

From the above reasoning it follows that, acrolein can be adsorbed in different ways on an acid–base catalyst depending on the types of sites it possesses; this in turn determines the selectivity of acrolein reduction on the catalyst [15].

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