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Hydrogenation of substituted acrolein over alumina supported ruthenium catalysts

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The gas phase hydrogenation of acrolein, 2-methyl-2-propenal, 2-butenal and 3-methyl-2-butenal was studied on Ru/Al_2O_3 and RuM/Al_2O_3 catalysts (M = Sn, Fe, Zn, Ge, Sb). The specific activity increases when the second element is added to the parent Ru/Al_2O_3 catalyst.This was ascribed to the activation of the C=O bond by $M^{\delta+}$ species. Tin is the only additive which promotes the allyl alcohol selectivity. When methyl groups are tagged on the C=C bond the selectivity to the unsaturated alcohol increased sharply due to the steric hindrance against the adsorption of the substrate via the C=C double bond.

Keywords: Ruthenium; bimetallics; hydrogenation; unsaturated aldehydes

1. Introduction

There is still a stimulating interest in hydrogenating α, β-unsaturated aldehydes to the corresponding unsaturated alcohols. There are several recent reports putting in evidence that the activity and selectivity of the supported metal for that reaction depend on the size of the metal particles [1–5], the nature of the supports and precursors [1,6–11], the occurrence of some "bimetallic" phase [6,11–18]. From these studies it emerges that the selectivity in the unsaturated alcohol is increased: (i) on large particles; (ii) when using a support acting as a macroligand favouring some electron transfer, like graphite; (iii) when some electropositive elements or species are present onto the surface of the catalyst, or in the first underlayer [15]. Moreover, the influence of particle size on selectivity which is large on cinnamaldehyde [2,3], is quite low on acrolein [4]. In order to get a better insight in this important class of reactions we have initiated a series of studies on the effects of particle sizes, support and alloying on the hydrogenation of α, β-unsaturated aldehydes over model supported Ru catalysts. As part of this programme, we report here the influence of alloying ruthenium with iron, tin, germanium, zinc, lead or antimony for

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acrolein hydrogenation, and the effect of steric hindrance from the substrate by reacting acrolein, 2-methyl-2-propenal, 2-butenal and 3-methyl-2-butenal.

2. Experimental

2.1. CHEMICALS

Hydrogen of high purity (99.99%) was used for the catalytic experiments and hydrogen of ultra-high purity (99.995%) for adsorption measurements. Acrolein, 2-methyl-propenal, 2-butenal and 3-methyl-2-butenal were the reactants. Ruthenium acetylacetonate, iron acetylacetonate, tetrabutyl tin, tetrabutyl germanium, tributyl antimony and diethyl zinc were used as precursors for the catalysts in order to avoid the effect of the residual ions which could affect the catalytic properties. The support for catalysts was γ-Al_2O_3 (Rhone Poulenc, 200 m^2/g).

2.2. CATALYST PREPARATION

The monometallic catalysts were prepared by adsorption of the acetylacetonate complex on the carrier. The requisite of the precursor was dissolved in benzene previously dried in zeolite 4 Å. The contact was maintained for 60 h before the solution was filtered. The solid was first dried overnight at ambient temperature and further under a stream of nitrogen at 423 K. Without exposing to atmosphere, the solids were reduced in a stream of diluted hydrogen (H_2/N_2, 20/80) at 573 K.

All the bimetallic catalysts were prepared starting from the pre-reduced parent Ru/Al_2O_3 catalyst. The Ru–Sn, Ge, Sb, Zn on alumina were prepared by using the controlled surface reaction method as described previously [19]. In short, the basic principle of this method constitutes in reacting the parent Ru/Al_2O_3 (reduced in situ before use) catalyst with desired amount of the $(C_4H_9)_4Sn$, for instance, in *n*-heptane solution under hydrogen. The reaction was carried out at 353 K. $Ru–Fe/Al_2O_3$ was prepared by impregnation of prereduced Ru/Al_2O_3 with $Fe(acac)_3$ in toluene. All the bimetallic catalysts were dried at room temperature under vacuum and then reduced at 573 K under pure H_2. All the samples were stored under air without any extra precautions.

The metal contents were determined from the UV absorbance of the precursor solutions before and after contact. For a few samples this was counterchecked by atomic absorption spectroscopy. The values determined by both methods were comparable.

2.3. CATALYST CHARACTERIZATION

The catalysts were characterized by hydrogen chemisorption and transmission electron microscopy.

The chemisorption of hydrogen was carried out in a static volumetric apparatus. The sample (500–800 mg) was reactivated in situ at 623 K under hydrogen stream overnight, then outgassed at the same temperature for 2 h at 3×10^{-3} Pa. For the ruthenium catalysts, the hydrogen chemisorption was performed following the method of Yang and Goodwin [20]. The hydrogen adsorption isotherms were determined in the range of 6.6–33 kPa at 373 K. After the first adsorption isotherm, the cell was degassed for 5 min at the same temperature and a second adsorption was carried out in the same manner. The difference between the two isotherms extrapolated to zero pressure gave the quantity of the irreversibly adsorbed hydrogen, stoichiometry of H_{irr}/Ru was assumed to be unity as per Yang and Goodwin [20]. The uptake of irreversibly adsorbed hydrogen allows us to determine the dispersion ($D = Ru_{surf}/Ru_{tot}$).

Some catalysts were examined by transmission electron microscopy (TEM) using a Jeol 100CX microscope. The agreement between the results of electron microscopy and hydrogen chemisorption for the parent Ru/Al_2O_3 catalyst is good. When adding the second element to Ru/Al_2O_3 there is no significant change in the mean size of metallic particles which remains around 1.5–2 nm. The sharp decrease of hydrogen uptake (table 1) is clearly related to the presence of the second element at the surface of bimetallic particles. This behaviour was expected from the small amounts of the second metal added and the protocole used to prepare the bimetallic samples [19].

2.4. CATALYTIC EXPERIMENTS

The catalysts prepared were studied for the hydrogenation of acrolein, 2-methyl-propenal, 2-butenal and 3-methyl-2-butenal in the gas phase. The reaction was carried out at atmospheric pressure in a microflow reactor operated at low conversion in order to avoid heat and mass transfer limitations. Hydrogen was passed through a saturator containing the reactant, into the glass reactor kept in a furnace at constant temperature. The reactor was provided with a preheater coil and the catalyst was supported on a porous glass disc. The effluents were analyzed

Table 1
Chemical composition and hydrogen adsorption of Ru/Al_2O_3 (1.1% Ru) and RuM/Al_2O_3 (M = Sn, Ge, Zn, Sb, Fe) catalysts

Catalyst	M	wt% M	M/Ru (at./at.)	H/Ru	Mean particle size from TEM (nm)
Ru/Al_2O_3	–	0.0	0.0	0.60	1.1
$RuSn/Al_2O_3$	Sn	0.29	0.25	0.20	1.2
$RuFe/Al_2O_3$	Fe	0.14	0.25	0.34	–
$RuGe/Al_2O_3$	Ge	0.17	0.25	0.29	–
$RuSb/Al_2O_3$	Sb	0.30	0.25	0.28	–
$RuZn/Al_2O_3$	Zn	0.16	0.25	0.28	–

on-line by a gas chromatograph. Carlo-Erba, equipped with a capillary column (30 m × 0.53 mm i.d., DBWAX bonded phase). The tubings from the reactor to the gas sampling valve were heated to prevent any condensation of the products. An aliquot (50–100 mg) of the sample used for chemisorption measurements was reactivated in situ under flowing hydrogen at 573 K overnight. The reactions were studied at 353 K.

The catalytic activity was expressed as a reaction rate in units of moles converted per second and per gram of catalyst, or as turnover frequency (TOF), number of reactant molecules transformed per hour and per surface Ru atom.

3. Results and discussion

In our previous study on the gas phase hydrogenation of acrolein over Ru/Al_2O_3 of widely varying dispersion [4] we quoted several points:

(1) At initial time, there was a significant selectivity to allyl alcohol when $P(H_2)/P(\text{acrolein})$ was around one. When this reactant molar ratio increased the initial selectivity to allyl alcohol decreased rapidly.

(2) There was an initial decrease of activity (70%) comparable with that reported for the gas phase hydrogenation of crotonaldehyde [9,21].

(3) Acetone was formed as an initial product; in order to explain this behaviour, we proposed that acetone was formed through a 1,4-diadsorbed intermediate on some electron-deficient sites which could be situated at the interface between the metal particles and Al_2O_3.

(4) Selectivity to allyl alcohol is only weakly modified by the ruthenium dispersion.

Thereafter, we have compared the monometallic and bimetallic catalysts under initial conditions and with $P(H_2)/P(\text{acrolein}) = 0.82$ as in the previous study [4]. Table 2 presents the main catalytic properties of the samples.

The first point which appears very clear is the promotion of activity by the sec-

Table 2
Catalytic properties of Ru/Al_2O_3 and RuM/Al_2O_3 (M = Sn, Ge, Zn, Sb, Fe) catalysts for the hydrogenation of acrolein at 363 K; $P(\text{acrolein}) = 11$ kPa, $P(H_2) = 9$ kPa, $P(N_2) = 81$ kPa

Catalyst	H/Ru	TOF (h^{-1})	Product selectivity (mol%)				
			propanal	acetone	allyl alcohol	propanol	lights
Ru/Al_2O_3	0.60	6.2	23.8	30.9	45.2	–	–
RuSn/Al_2O_3	0.20	25.7	34.5	–	52.7	5.5	7.2
RuFe/Al_2O_3	0.34	27.9	57.3	–	42.7	–	–
RuGe/Al_2O_3	0.29	45.5	71.4	–	17.1	9.2	7.1
RuSb/Al_2O_3	0.28	53.1	74.8	–	7.1	7.1	11.0
RuZn/Al_2O_3	0.28	45.8	75.5	–	7.4	4.4	12.6

ond element, the turnover frequency was increased by a factor of 5 to 9 depending on the promoter. This is fully in line with the previous reports on the promoting effect of Fe and Sn [6,14–16]. It is generally proposed, in these reports, that the electropositive metal (Fe) or ionic species ($Sn^{\delta+}$) polarizes the C=O bond, making it more reactive towards the hydrogen attack. However, Beccat et al. [15], by studying the hydrogenation of crotonaldehyde and 3-methyl-2-butenal over Pt(111) and $Pt_{80}Fe_{20}(111)$ single crystals claimed that the absence of Fe in the surface layer of PtFe in the course of the reaction showed that a direct interaction between iron and the carbonyl group is not necessary to enhance the selectivity. They proposed an electronic modification of the Pt in the first surface layers when alloying with Fe. Taking into account this explanation for the enhancement of activity, one could guess that in parallel a higher selectivity to allyl alcohol will result. Actually, this is only true for the $RuSn/Al_2O_3$ sample. Tin was known to be the best promoter for allyl alcohol selectivity for hydrogenation of acrolein over Pt catalysts [18] under different reaction conditions. By contrast, on RuGe and RuZn catalysts the selectivity to propanal is sharply increased, and RuFe exhibits an intermediate behaviour. In other respect, a point which calls forth a particular attention is the disappearance of acetone formation on the bimetallics. The acetone would be formed by 1,4-adsorption, at both C=C and C=O double bonds [4]. This adsorption of the conjugated system leads to allyl alcohol on the one hand, and propanal or acetone on the other hand. Acetone formation occurring at some specific interfacial sites at the periphery of the metal particles. The addition of Sn, Ge, Sb, Zn or Fe to Ru inhibits these sites, resulting thus in an enhancement of propanal selectivity. Thereupon, even if the C=O bond is activated by Fe, Zn, Ge or Sb addition, the C=C–C=O conjugated system interacts very likely as a single entity with the Ru surface. Tin alone tends to decrease the interaction between C=C and Ru orients the reaction towards allyl alcohol. Anyway, it appears difficult to increase the selectivity to allyl alcohol by acting on the Ru phase only. It was then postulated that steric factors from the incoming reactant could control the selectivity.

The hydrogenation of acrolein, 2-methyl-propenal, 2-butenal and 3-methyl-2-butenal was then studied on Ru/Al_2O_3 at lower substrate pressure, $P(H_2)/P(\text{substrate}) \approx 7–8$. The relative rates for hydrogenating the C=O versus the C=C bond are reported in fig. 1 for the various reactants. The great influence of substituting one or two hydrogen atoms by a methyl group appears immediately, since the relative rate between the two double bonds is multiplied by 100. The Lebedev rules [22] state that the reactivity of C=C double bonds for hydrogenation decreases with the substitution on carbon atoms. It has been shown that this behaviour is not due to a lower reactivity of the C=C bond in the adsorbed state, but is better explained by a decrease of the adsorption constant when the molecule becomes more and more hindered [23]. This is certainly the prevailing factor for the hydrogenation of substituted acrolein on small Ru particles. It is interesting to note that the relative reactivity between C=O and C=C bonds is one order of mag-

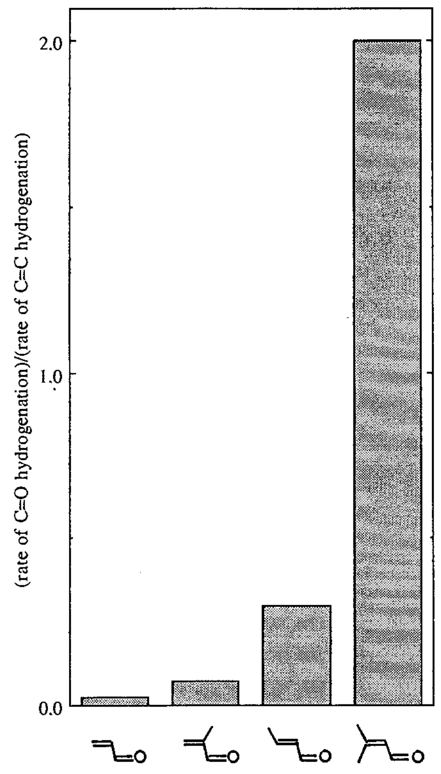

Fig. 1. Relative reactivities between the C=O and the C=C bonds for hydrogenation of substituted acrolein over Ru/Al_2O_3 catalyst (H/Ru = 0.60); $P(H_2)/P(\text{substrate}) \approx 7$–$8$, $T_R = 363$ K.

nitude larger for 3-methyl-2-butenal than for 2-butenal; the same difference is reported by Beccat et al. [15] for the hydrogenation of 3-methyl-2-butenal and 2-butenal over Pt(111) or $Pt_{80}Fe_{20}(111)$ single crystals.

It appears that the key factor governing the selectivity to unsaturated alcohol in α, β-unsaturated aldehydes hydrogenation is the tilting of the alkyl chain far from the surface; this factor is more important than activation of the C=O bond by electron deficient species for instance, which encounters some difficulties to favour the selectivity to unsaturated alcohol if the reactant can adsorb as a flat species. In this respect, among the various modifiers we added to Ru, Sn is the only one which depresses the chemisorption strength between C=C and the Ru surface. As a first step, the interaction between the C=C double bond and Ru will occur by an "electron donation" between the π orbitals of C=C and the 4d hole of Ru. It was shown by various approaches that something like an "electron transfer" occurs from Sn to Pt, Rh, Pd or Ni. If the same is postulated for RuSn bimetallic aggregates, some filling of the 4d Ru orbitals would explain the lower interaction between Ru and the C=C double bond.

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