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A new method to prepare highly dispersed supported metal catalysts

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On a solid surface the effects of the implosion of the bubbles, created during a sonication run, are commonly used to clean or to erode the surface itself. In the present work, ultrasound was used in order to obtain a ruthenium on alumina catalyst distinguished by a very high value of the dispersion of the metal. The samples were characterized with different techniques in order to study the influence of the sonication on both the metal crystallites and the support.

Keywords: Preparation; ultrasound; ruthenium catalysts; high dispersion

1. Introduction

The progression of a sound wave in a liquid phase causes the molecules of the solvents to oscillate about their mean position. During the compression and rarefaction cycles, the average distance between the molecules may decrease and increase respectively. It is possible, when a large negative pressure is applied to the liquid, that such an average distance may exceed the critical molecular distance and the liquid phase may break down forming some cavitation bubbles [1]. The effects of the implosion of the cavitation bubbles generate high energy shock waves with pressures of several thousands of atmospheres; moreover, near the surface of a solid, the collapse of the liquid phase causes a microstreaming of a jet of solvents hitting the surface with a very high velocity, sometimes estimated to be as high as 100 m s^{-1}. These effects usually lead to the removal of passivating surface coatings, to the creation of surface defects and also to the reduction of particles size [1,2].

In a recent work [3], it had been shown that ultrasound plays a relevant role in preparing highly dispersed pure amorphous iron. The aim of the present work was to increase the dispersion of ruthenium supported onto alumina catalysts by means of ultrasound (US).

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All the samples were characterized in order to study the influence of the sonication on both the metal crystallites and the support. Moreover, some chosen catalysts were used in a laboratory plant studying the Fischer–Tropsch synthesis ($CO + H_2 \rightarrow$ hydrocarbons). It is well known [4–9] that this is a structure sensitive reaction, which means that the turnover rate (mol CO converted (g-atom surface metal)$^{-1}$ s^{-1}) [10], the olefin/paraffin ratio and the chain growth probability were found to be influenced by the metal particles size.

2. Experimental

The catalysts were prepared in a particular instrument following a wet imbibition method in vacuum [11], using two different ruthenium precursors, $RuCl_3$ and $Ru(acac)_3$, and a commercial alumina (AKZO, grade E-C, surface area (BET): 159 m^2/g, particle diameter 6×10^{-5} m). The catalysts were prepared varying the amount of the ruthenium from 0.5 to 5 wt%. The support was outgassed at 473 K for 2 h at a pressure of about 10 Pa in order to free all the pores from the adsorbed water and air. Then, always in vacuum, the ruthenium salts, solved in suitable solvents (water for $RuCl_3$, toluene for $Ru(acac)_3$) were admixed with the support at 273 K. The samples were dried, under vacuum control, at 360 K and then calcined in air at 523 K for 2 h.

The sample was then divided into two batches and reduced with an aqueous solution of hydrazine (N_2H_4) at 340 K. A first batch was usually reduced putting in a certain amount of sodium bicarbonate that is necessary to have a pH higher than 6. This pH value is essential to allow the hydrazine decomposition reaction: $N_2H_4 \rightarrow N_2 + H_2$ [12]. The second batch was reduced using the same procedure but after the addition of N_2H_4, the solid–liquid suspension was sonicated (Branson – B12, frequency 20 kHz, power 30 W – calculated with the calorimetric method [13]). This particular power was chosen in order to minimize the possible effects of destruction of the support [1,2]. In fact, increasing the power it was possible to

Table 1
Dispersion data (%) obtained by the chemisorption technique for catalysts prepared without ultrasound (no US) and with ultrasound (with US)

Metal (wt%)	Precursor	Metal dispersion (%) no US	Metal dispersion (%) with US
0.5	$Ru(acac)_3$	37	66
1	$Ru(acac)_3$	34	60
3	$Ru(acac)_3$	25	35
5	$Ru(acac)_3$	20	22
1	$Ru(Cl)_3$	12	31
5	$Ru(Cl)_3$	23	20

observe the transformation of the alumina in fine powder, losing all its morphological structure.

The metal dispersion was characterized by a particular H_2 chemisorption technique, coupling the single introduction and back-sorption classical methods [14,15]; then the samples were characterized by XPS (M-Probe-SSI, monochromatic Al Kα source) and by XRD (Rigaku diffractometer).

The possible changes in the support were detected by BET analysis (Carlo Erba Strumentazioni) and by SEM (Cambridge Stereoscan 150).

3. Results and discussion

In table 1 the summarized data of the metal dispersion obtained by the chemisorption technique are shown. As it can be observed the samples prepared from $RuCl_3$ show a lower dispersion value. In fact, the chlorine atoms bind themselves to the metallic sites on the surface of the support and forbid the hydrogen to chemisorb itself on the metal [16]. This situation prevents a correct measurement of the dispersion of the ruthenium and the resulting value is lower than the real value since a part of the metal is not correctly considered.

In order to compare the dispersion data on the whole, it is possible to calculate the increment of the metal dispersion (ID% = [(metal dispersion with US – metal dispersion without US)/ (metal dispersion without US)] ×100), due to the use of ultrasound, from the sample with low amount of ruthenium (0.5%) to the sample with a high amount (5%) (fig. 1). From these quantitative data, it is actually underlined the ultrasound benefits; in fact, especially when the amount of ruthenium is rather low (0.5–1%), the dispersion value of the sonicated sample is much higher than the value obtained from the catalyst prepared with the same metal amount, but without using ultrasound during the reduction step.

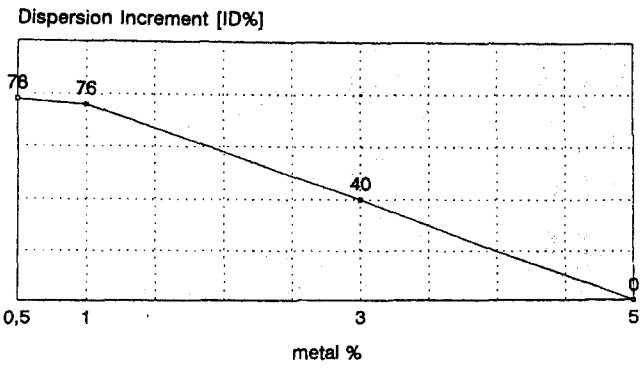

Fig. 1. Increment of Ru metal dispersion due to the use of ultrasound, calculated for the samples from $Ru(acac)_3$.

In all the samples, the crystalline structure of both the support and the metal is maintained even after the sonication and this was verified by XRD analysis. The recorded spectra showed really sharp and very defined lines that are typical of a crystalline structure.

The XPS analysis (M-Probe-SSI, monochromatic Al Kα source) of these samples pointed out a decrease in the amount of metal species on the surface of the support comparing the catalyst reduced with and without ultrasound. In order to understand this phenomenon, a qualitative measurement was carried on: another sample was prepared, following the same procedures as mentioned above, but using another alumina with larger particles (Martin Werke, surface area (BET): 185 m^2/g, particle diameter 4×10^{-3} m). As before, a part of the batch was reduced under sonication and the other part only with hydrazine. A grain of the supported alumina was then dissected and by optical microscope (Nikon) it was possible to observe the higher penetration of the metal in the catalyst reduced with ultrasound (fig. 2a) than the catalyst reduced without (fig. 2b), suggesting that the ultrasound may cause a distribution of the metal in the support as in the case of an inner shell catalyst [17].

CATALYSTS TESTING

The catalyst was loaded into a fixed-bed reactor and in situ reduced under H_2 flow at 8×10^5 Pa to 623 K, in spite of the pre-reduction step with hydrazine during the preparation of the sample. After this treatment, the reaction started at a pressure of 5×10^5 Pa at 508 K with a mixture of H_2 and CO (2 : 1, molar ratio) and a

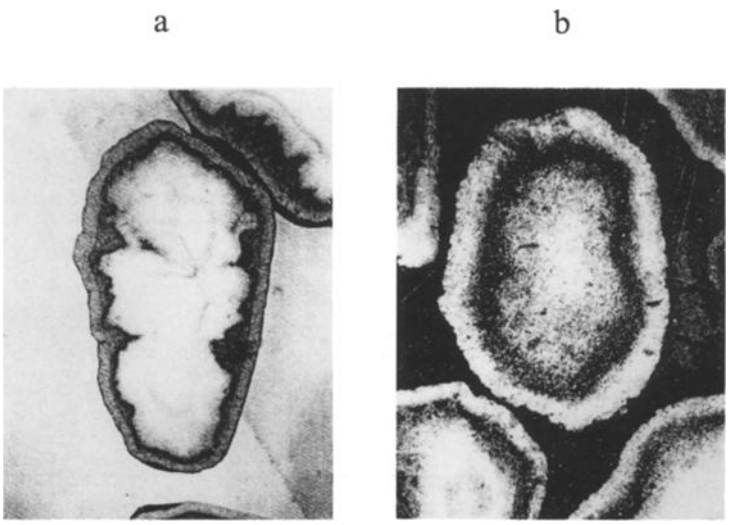

Fig. 2. Optical microscope micrographs of a section of a grain of sample (Ru 1% from $RuCl_3$ on alumina): (a) sample reduced only with hydrazine; (b) sample reduced with hydrazine and with the help of ultrasound.

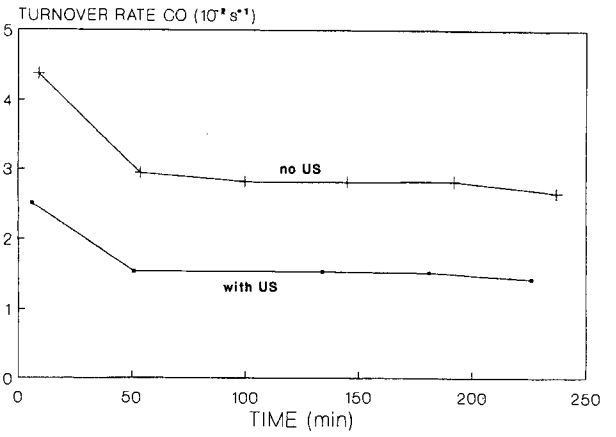

Fig. 3. The CO turnover rate (mol CO converted (g-atom surface metal)$^{-1}$ s^{-1}). Experimental conditions: $P = 5 \times 10^5$ Pa; $T = 508$ K; SV = 53.5 mmol CO/(min g_{Ru}); $H_2/CO = 2/1$ molar.

space velocity (SV) of 53.5 mmol Co/(min g_{Ru}). All the products from the reactor were separated in a wide bores column (Chrompack) ($\phi = 53 \times 10^{-5}$ m, $L = 10$ m). After this separation, the gases are analyzed in a gas-chromatograph (HP-5890) with a thermoconductivity detector.

The CO conversion (calculated from a mass balance on the amount of carbon in CO and of all the hydrocarbons, revealed from the detector of the gas-chromatograph), the selectivity to olefins (C_2–C_4) and the production of C_5–C_{13} hydrocarbons were investigated.

Studying the reactivity of the samples prepared from Ru(acac)$_3$ (table 1), it was observed that all the experimental data agreed with the recent literature data. In

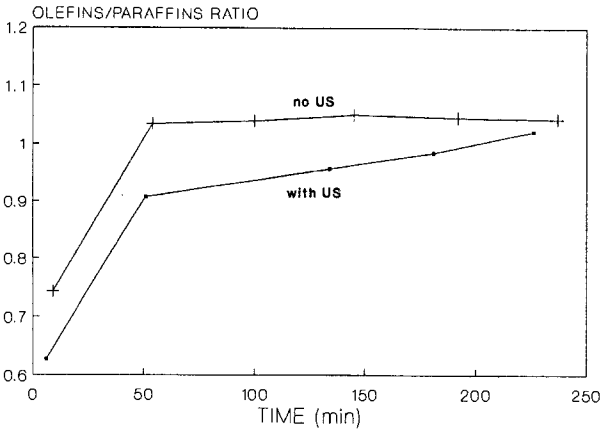

Fig. 4. The olefins/paraffins ratio (calculated as $(C_2^= + C_3^=)/(C_2 + C_3)$). Experimental conditions as in fig. 3.

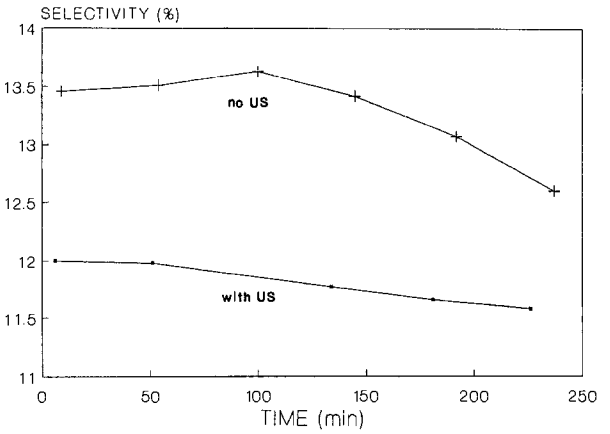

Fig. 5. The C_5–C_{13} selectivity. Experimental conditions as in fig. 3.

particular, it has been possible to confirm that increasing the dispersion of the metal particles, the following variables decrease:

- the CO turnover rate (fig. 3) [6–10,18];
- the olefins/paraffins ratio (calculated as $(C_2^= + C_3^=)/(C_2 + C_3)$) (fig. 4) [6,10,18];
- the C_5–C_{13} selectivity (fig. 5) [6,7,10,18].

Moreover, also observed was a decrease of the chain growth probability factor (α) from the sample with high dispersion ($\alpha = 0.69$) in comparison with the sample with low dispersion ($\alpha = 0.74$).

4. Conclusion

The samples prepared using ultrasound during the reduction step produced the very high increase of the dispersion of the metal on the support, especially for catalysts with a low amount of metal (0.5–1 wt%). On large support particles, a different distribution of active metal may be produced (inner shell catalysts).

The power of the ultrasound, used during the preparation of the samples, is the limiting point of the method. In fact, it is necessary to work with a suitable power in order not to destroy the support.

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