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New findings on soybean and methylester epoxidation with alumina as the catalyst

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The activity of a commercial alumina, after a preliminary characterization, was investigated in epoxidation with soybean oil with aqueous hydrogen peroxide. Results show that the γ-alumina was an efficient catalyst. The role of the solvent in the epoxidation reaction in the presence of alumina was investigated. A "no-innocent" solvent role was demonstrated. Moreover, the optimization of the methyl oleate epoxidation reaction with alumina was eventually valuated, varying the type of the solvent and concentration of hydrogen peroxide in order to obtain a product with commercial features.

1. Introduction

The epoxidation reaction of vegetable oils and their derivatives has attracted increasing interest from both the scientific and industrial community, because the obtained epoxides are important building blocks for the preparation of chemical intermediates, which are the basis for a wide variety of consumer products. They are used directly as plasticizers and stabilizers for PVC resins, as additives in lubricants, and as components in plastics. On the industrial scale, oil epoxidation is currently performed through the "Prileschajew reaction", where the unsaturated oils react with a percaboxylic acid, such as peracetic or performic, obtained *in situ* through the acid catalysed oxidation of the respective organic acid with hydrogen peroxide.[1] The soluble mineral acids, such as H_3PO_4 and H_2SO_4, are commonly used as catalysts. However, the use of these acids involves problems concerning the selectivity of the process, because they promote the degradation reaction of the produced epoxides, with the formation of detrimental side products. The presence of such by-products, derived by side reactions, in the commercial epoxidized oils diminishes their attractiveness as starting materials for further syntheses. Moreover, there are other severe limitations correlated to this technology, such as the disposal of salts derived from the final neutralization of mineral acids, the corrosion and expensive separation operations.[2] Therefore, the setting up of new sustainable processes based on the use of green reagents and clean technologies is imperative to overcome the afore mentioned disadvantages.

For the epoxidation reaction, the use of hydrogen peroxide as oxidant and a heterogeneous catalyst is attractive, because in this case the water would be the only by-product (Fig. 1), and the catalysts could be easily recovered at the end of the process. Moreover, the use of a heterogeneous catalyst could allow to suppress the oxirane ring opening side reactions, considering the lack in free acidity in the reaction environment (Fig. 1).

Many different catalytic systems for epoxidation, using hydrogen peroxide as oxidant, have been studied and proposed in literature.[3,4] Among them, the titanium silicalite (TS-1) was reported as a milestone for the oxidation of olefins with hydrogen peroxide.[5] However, this catalyst is barely active with large substrates like oils and methyl esters, due to the small pores diameter (5.6 × 4.7 Å) of TS-1. Extensive work was done to incorporate Ti(IV) in large molecular sieves pores, leading to materials such as Ti-MCM-41 and Ti-MCM-48.[6] Recently, some niobium–silica based solids were developed and reported in literature as active catalysts for the epoxidation reaction.[7–10] It was demonstrated that different synthesis procedures lead to the presence of different structures and surface distribution of active sites, influencing in this way the activity and selectivity in the epoxidation reaction. However, the majority of the catalysts

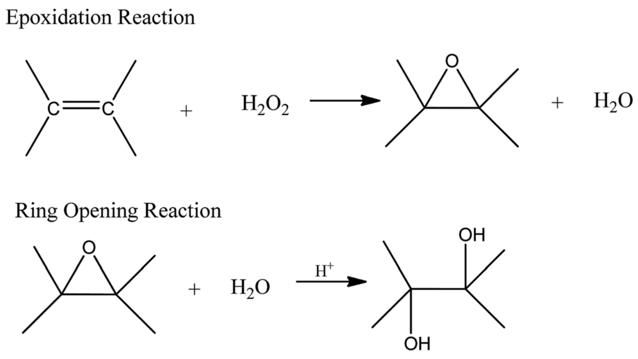

Fig. 1 Epoxidation and ring opening reactions.

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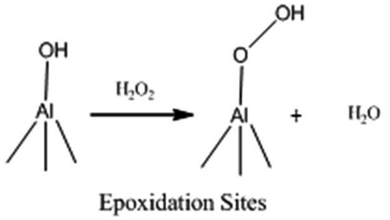

Scheme 1

based on transition metals are expensive due to their complex synthesis. Therefore, the use of no expensive catalyst could be attractive from the commercial point of view.

The γ-alumina was found to be able to activate the hydrogen peroxide for the oxidation, through the formation of a peroxide site, according to the reaction reported in Scheme 1.[11,12]

As a matter of fact, a good activity and selectivity towards different epoxides was reported.[13,14] A moderate performance was also found with methyl esters.[15] However, only preliminary data was reported for the epoxidation of bulk substrates such as oil.[16] Therefore, the aim of this work was to carry out a detailed study on the activity of γ-alumina in the soybean oil and methyl esters epoxidation reaction with hydrogen peroxide. Although the use of alumina in epoxidation is not new, the evaluation of its activity with larger organic substrates represents a novelty in this field. For this purpose a commercial alumina, after a preliminary characterization, was tested in epoxidation with soybean oil and the role of the solvent in the epoxidation reaction in the presence of alumina was investigated. Some crucial aspects for the epoxidation reaction were investigated, such as the type of the solvent, the type of substrate, the concentration of hydrogen peroxide.

2. Experimental procedures

2.1. Materials

Commercial alumina, supplied by Fluka (neutral, activated aluminum oxide for chromatography, Brockman activity I, particle size of 0.05–0.15 mm), was used, as received, in the epoxidation tests. Methyl oleate, (acidity number of 0.64 $\mathrm{mg_{KOH}\ g_{sample}}^{-1}$) ethyl acetate, acetonitrile and toluene were supplied by Sigma Aldrich and were used as received, without further purification. Soybean oil, (iodine number of 128 $\mathrm{g_{I_2}\ g_{sample}}^{-1}$ and acidity number of 0.36 $\mathrm{mg_{KOH}\ g_{sample}}^{-1}$), was purchased in a local food store. The hydrogen peroxide (54.9% wt) was kindly provided by Solvay S.p.A.

2.2. Catalyst characterization

The X-Ray Diffraction (XRD) patterns were determined with a Philips 1887 diffractometer, using Cu Kα radiation in a 5–80° 2θ range and at a scan velocity of 0.02° $2\theta\ \mathrm{s}^{-1}$. The specific surface area of the alumina was determined by the BET method,[17] using nitrogen adsorption isotherms (at 77 K) in a Sorptomatic 1990 instrument. X-Ray Fluorescence (XRF) analysis on the raw materials was performed through a BRUKER Explorer S4 apparatus.

2.3. Epoxidation reaction

The epoxidation reactions were carried out in a round-bottom glass batch reactor (100 mL), put in an oil bath, equipped with a condenser, a thermometer and a magnetic bar for vigorous stirring (300 rpm). The temperature was kept constant (≈80 °C). In a typical experiment, 600 mg of catalyst, 20 cm^3 of solvent, 5 g of organic substrate and 6.9 g of hydrogen peroxide (54.9% wt) were used. All the reagents were added in one pot at the beginning of the reaction. The reaction was conducted in general for 5 h. Operating conditions different from the reference ones will be detailed in the forthcoming text. The final solution was separated from the catalyst by filtering, and it was analyzed to evaluate the double bonds conversion and the selectivity to oxirane rings, determining the Iodine Number (I.N.) and the Oxirane Number (O.N.) according to the analytical methods reported in the literature.[18,19]

2.4. Hydrogen peroxide decomposition

The decomposition reaction was conducted in the same batch reactor used for the epoxidation reactions. To this end, 6.9 g of H_2O_2 were fed to the reactor preloaded with 600 mg of catalyst. The system was heated to reflux temperature of solvent (ethyl acetate) and placed under continuous stirring (360 rpm) for 5 h. Intermediate samples were collected, and cooled in a bath of water and ice. The amount of decomposed hydrogen peroxide was assessed by iodometric titration according to the method described in ref. 2.

3. Results and discussion

3.1. Alumina characterization

The XRD analysis and the comparison with the standard JCPD card (00-010-0425) confirmed the presence of γ phase for the investigated alumina. Its textural properties were determined by nitrogen adsorption–desorption isotherm at 77 K. An adsorption isotherm of type IV was observed, and the type of hysteresis loop indicates the presence of ink bottle-shaped mesopores. As reported in Table 1, values of specific surface area and pore volume equal to 149 $\mathrm{m^2\ g^{-1}}$ and 0.27 $\mathrm{cm^3\ g^{-1}}$ were obtained, respectively. The mean pore diameter is about 4.2 nm.

The chemical composition was determined by XRF and indicates the main presence of alumina, together with a low amount of other impurities (Table 1).

3.2. Epoxidation of soybean oil

3.2.1. Activity of alumina and effect of hydrogen peroxide decomposition. Table 2 reports in detail the operating conditions adopted for each of the 16 epoxidation tests whose results are reported in this paper. Tests varied with each other in terms of substrate nature and amount, type of solvent, amount of H_2O_2, amount of alumina, reaction time. Table 2 lists the conversion and selectivity experimental results. They pointed out that alumina is an active catalyst in epoxidation with hydrogen peroxide, also in the presence of a more bulky substrate like oil. In fact, using ethyl acetate as solvent (Run #1) a conversion of double bonds of 56% and a selectivity to oxirane

Table 1 Principal characteristics of alumina

	BET surface (m^2 g^{-1})	Mean pore diameters (nm)	Pore volume (cm^3 g^{-1})	Chemical composition (% wt)							
				CaO	SiO_2	Al_2O_3	K_2O	Fe_2O_3	Na_2O	L.o.i.[a]	Others
Fluka	149	4.2	0.27	—	0.11	90.37	0.12	—	0.32	7.00	1.67

[a] Loss on ignition @ 900 °C.

Table 2 Operating conditions adopted for the epoxidation reaction at 80 °C (in any case, 20 cm^3 of solvent were used), and related conversion and selectivity results

Run	Substrate	Solvent	H_2O_2 54.9% wt (g)	Substrate (g)	Alumina (g)	Reaction time (h)	Conversion[a] (%)	Selectivity[b] (%)
1	Soybean oil	Ethyl acetate	6.9	5.0	0.6	5	56	59
2	Soybean oil	Ethyl acetate	6.9	5.0	0.6	10	75	64
3	—	Ethyl acetate	6.9	—	0.6	5	78[c]	—
4	Soybean oil	Ethyl acetate	6.9	5.0	—	5	0	—
5	—	Ethyl acetate	6.9	—	0.6	2.5	65[c]	—
6	Soybean oil	Solution of Run 5	—	5.0	—	2.5	11	41
7	Methyloleate	Ethyl acetate	6.9	5.0	0.6	5	57	71
8	Methyloleate	Acetonitrile	6.9	5.0	0.6	5	72	81
9	Methyloleate	Toluene	6.9	5.0	0.6	5	22	7.0
10	Soybean oil	Acetonitrile	6.9	5.0	0.6	5	6.7	4.3
11	—	Acetonitrile	6.9	—	0.6	2.5	—	—
12	Methyloleate	Solution of Run 11	—	5.0	0.6	2.5	0	—
13[d]	Methyloleate	Acetonitrile	6.9	5.0	0.6	5	75	58
14	Methyloleate	Acetonitrile	6.9	5.0	0.6	8	71	74
15	Methyloleate	Acetonitrile	8.1	5.0	0.6	5	70	77
16	Methyloleate	Acetonitrile	6.9 + 3.4[e]	5.0	0.6	8	80	96

[a] Conversion of double bonds. [b] Selectivity to oxirane rings. [c] Conversion of H_2O_2. [d] At the beginning of the reaction 0.1 g of glacial acetic acid was added. [e] After 5 h of reaction. The standard deviations relative to conversion and selectivity values are 2.8% and 1.8% respectively.

of 59% were found after 5 h of reaction. These results are in good agreement with those reported by Suarez *et al.*[20] for the methyloleate epoxidation reaction, obtained with an alumina having similar specific surface area (167 m^2 g^{-1}). The activity of alumina was also studied for longer times in epoxidation reaction (Run #2), obtaining a profile of conversion and selectivity as shown in Fig. 2. It emerges that the reaction is stopped at around 75% of conversion (10 h as reaction time), where a selectivity of 64% was observed, notwithstanding the use of an excess of hydrogen peroxide (molar ratio hydrogen peroxide/double bonds = 4). The limit in the conversion could be due to a loss of hydrogen peroxide ascribable to the parallel decomposition reaction, because the alumina could also catalyze the hydrogen peroxide decomposition.[21] Regarding this aspect, a specific test has been also performed to evaluate the H_2O_2 decomposition in the presence of Al_2O_3 (Run #3, no substrate). The obtained results are also reported in Fig. 3. As it can be seen, H_2O_2 gradually decomposed up to 78% with respect to the initial amount in 5 h, and this explains the strong loss of activity along with the reaction time. In fact, as long as the epoxidation goes on, the reactive system loses a part of the oxidant useful for the reaction and it enriches in water, which is able to hydrolyze the oxirane ring. These results are in agreement with those by Sheldon *et al.*,[12] who pointed out the key role of the water amount on the epoxidation rate. Actually, a small amount of water is necessary to rehydrate the surface, indispensable for the activity of alumina in this reaction. However,

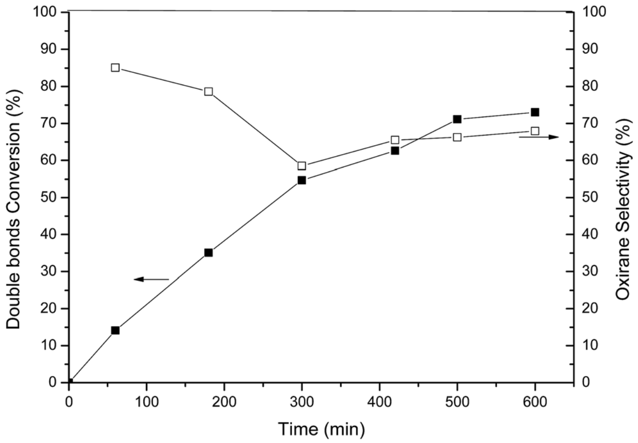

Fig. 2 Performance (conversion and selectivity) of the γ-alumina catalyst as a function of reaction time in the epoxidation of soybean oil. Operating conditions are those for Run #2 (Table 2), with a H_2O_2/double bonds molar ratio equal to 4. The standard deviations relative to conversion and selectivity values are 2.8% and 1.8% respectively.

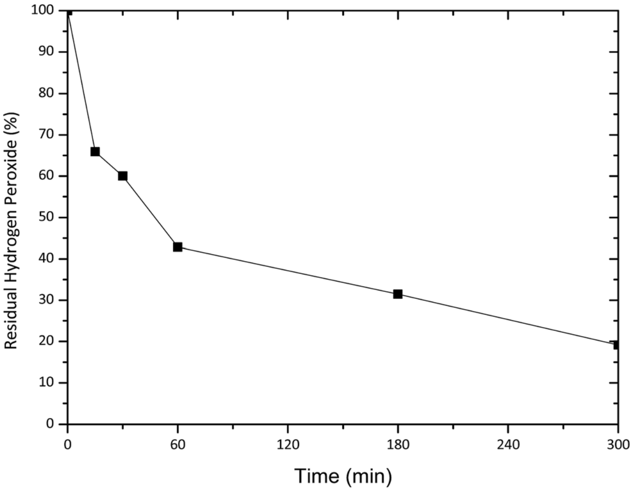

Fig. 3 Hydrogen peroxide decomposition as a function of reaction time in presence of γ-alumina catalyst. Operating conditions are those for Run #3 (no substrate, Table 2), with a H_2O_2/double bonds molar ratio equal to 4.

an excessive quantity of water, derived by the reaction and the use of dilute hydrogen peroxide, diminishes the selectivity to the desired epoxides.

One way to limit this problem may consist in the adding drop-by-drop the H_2O_2 to the reaction mixture, or gradually remove water.[22,23]

3.2.2. Role of the solvent. Practically, all the literature works concerning the application of γ-alumina as epoxidation catalyst report the use of a reaction solvent such as ethyl acetate. The detection of the characteristic odour of acetic acid in the final product of the epoxidation reaction, in the presence of ethyl acetate as solvent, led to the hypothesis that at the reaction temperature under investigation (80 °C) and in the presence of water coming from hydrogen peroxide, alumina could promote the hydrolysis of ethyl acetate to acetic acid. The formation of acetic acid was confirmed by titration of solvent in Run #3 with a KOH solution and qualitatively by gas chromatographic analysis. The solvent acidity at the beginning of the reaction was 0.39 $\text{mg}_{\text{KOH}}\ \text{g}_{\text{sample}}{}^{-1}$ while at the end it became 2.8 $\text{mg}_{\text{KOH}}\ \text{g}_{\text{sample}}{}^{-1}$.

This assumption can be explained considering the complicated alumina surface with the presence of different types and strengths of Lewis acid sites, which consist in form of coordinatively unsaturated aluminium ions and of different hydroxyl groups.[24] A lot of studies on this aspect with a large variety of techniques such as solid state NMR,[25–27] FT-IR[28,29] and theoretical calculations[30] have revealed the presence of three-, four- and five coordinate Al ions as Lewis acid sites, and up to or more than five types of surface hydroxyls for the dehydrated aluminas. Most of them are very weak acids and only one has been shown to be the most reactive. The epoxidation reaction was believed to take part on the alumina surface through the formation of hydroperoxo species, involving only weak Lewis acid sites, which consist in 5-coordinate Al^{3+}. The strong and medium Lewis acid sites are probably involved in undesired side reactions, such as the decomposition of hydrogen peroxide and the hydrolysis of ethyl acetate to acetic acid.[12]

Acetic acid can react with oxirane ring or catalyze the reaction of water with oxirane rings (ring opening), reducing the final yield. Moreover, because of the highly oxidizing environment, it can be argued that acetic acid forms peracetic acid, which could then react with the double bonds in the oil, *via* Prileschajew reaction, increasing the reaction rate of double bond epoxidation. To verify these assumptions, dedicated tests (Runs #4–6) were carried out. In particular, Run #4 was performed under the same conditions of Run #1, but without catalyst. No reaction of double bonds was observed. Run #5 was performed under the same conditions of Run #3 (no soybean oil), but the reaction was stopped at 2.5 h. Then, after the removal of alumina, the soybean oil was added and the reaction was carried out for other 2.5 h (Run #6). A conversion of 11% and a selectivity of 41%, obtained in this case, can be attributed to the reaction of formed peracetic acid with double bonds.

3.3. Methylesters epoxidation

The epoxidation reaction was also performed in ethyl acetate using methyl oleate instead of soybean oil as substrate (Run #7), under the same reaction conditions of Run #1. Notwithstanding the methyl oleate has a smaller dimension than that of triglycerides of soybean oil (methyl oleate has a molecular diameter of 2.5 nm while the dimensions of triglycerides fall in the range of 2.5–5 nm (ref. 33 and 34)), the same conversion of double bonds (around 56–57%) was found for the two reagents. This behaviour can be justified considering that the dimensions of the two reagents are comparable with the mean pore diameter of the catalyst (4.2 nm), and so relevant diffusive restrictions have not been observed.

The selectivity to oxirane in the case of methyl oleate (Run #7) is higher than the one obtained with soybean oil (Run #1) (71% *vs.* 59%). This behaviour can be justified by the presence in soybean oil of a high concentration of dienes and trienes, with the resulting oxirane rings being more reactive than in the case of monoenes.[31]

With the aim to optimize the synthesis of epoxidized methylesters, the effect of the solvent was further investigated. To this end, two other solvents with different polarity in respect to ethylacetate ($\varepsilon \approx 6.0$) were tested: acetonitrile ($\varepsilon \approx 37$) and toluene ($\varepsilon \approx 2.4$) (see Table 2). The largest values of double bonds conversion (72%) and selectivity to oxirane rings (81%) were obtained with acetonitrile (Run #8), while the worst results were obtained using toluene as solvent (Run #9, double bonds conversion = 22%; selectivity to oxirane rings = 7%). This result can be explained considering the better solubility of both epoxidation reactants in acetonitrile (methyloleate and hydrogen peroxide), with respect to the other two solvents. In particular, while the methyloleate is miscible in all solvents, hydrogen peroxide and water are completely soluble in acetonitrile, only partially in ethyl acetate and very poorly in toluene.[32] Moreover, the lower selectivity found when ethyl acetate as solvent was employed (with respect to the acetonitrile case) can be explained assuming the presence of acetic acid, derived by hydrolysis of ethyl acetate, as discussed above. This acid promotes the degradation of oxirane groups by ring opening reaction.[12,31]

The importance of the solvent choice can be further appreciated considering the results of Run #10, where acetonitrile was used as solvent in epoxidation reaction of soybean oil. The obtained result was worst than in the case of ethyl acetate (Run #10: double bonds conversion = 6.7%; selectivity to oxirane rings = 4.3%). This behaviour can be explained considering that oil is poorly dissolved in acetonitrile. Acetonitrile fills most of pore volume and therefore hinders the access of the triglyceride to reactive sites of the catalyst.

However, in the presence of acetonitrile as solvent the hydrolysis by hydrogen peroxide (Radziszewski reaction) to form peroxycarboximidic acid could be feasible, even if an alkaline environment is required.[35] Because epoxidation of methyl oleate is conducted in neutral reaction medium, the solvent hydrolysis should not occur. To confirm this, a run without substrate using acetonitrile as solvent was performed (Run #11) for 2.5 h. Alumina was then removed from the reaction solution and methyloleate was added (Run #12). No reaction of double bonds was observed after additional 2.5 h.

To further demonstrate the "non innocent" role of ethyl acetate a new run (Run #13) with the same condition of Run #8 was performed with adding 0.1 g of glacial acetic acid.

The results are in agreement with the forecasting. As a matter of fact, we observed a light increase in activity (conversion 75% instead 72%) but also a great decrease in selectivity (58% instead 81%).

Considering the interesting results found for the epoxidation of methyloleate in acetonitrile, we have investigated in detail this system. Extending the reaction time from 5 to 8 h (Run #14 *vs.* Run #8), the conversion does not further improve, while the selectivity gets a little worse (74% *vs.* 81%). This behaviour can be justified as in the case of soybean oil epoxidation in ethyl acetate with hydrogen peroxide decomposition.

The initial amount of used hydrogen peroxide was increased (from 6.9 to 8.1 g) to obtain a higher final conversion, but without success (Run #15 *vs.* Run #8). To further investigate this aspect, after 5 h of reaction hydrogen peroxide was added (50% of the amount initially charged, Run #16). The reaction appeared to restart, and after further 3 h high conversion (80%) and selectivity (96%) were achieved. These results confirm that the catalyst is still active and the stop of the reaction is due to the decomposition of hydrogen peroxide.

It is to point out that the obtained results are very interesting also from a practical point of view. As a matter of fact, the maximum selectivity generally obtained in epoxidation of methylesters reported for the Prileschajew reaction is around 80%, requesting more drastic conditions.[31] The obtained results are also better than those reported in the literature for epoxidation of methyl oleate with hydrogen peroxide catalysed by alumina but using ethyl acetate as solvent.[15,20]

4. Conclusions

In this work, it is shown that common commercial alumina is active in the epoxidation of soybean oil with aqueous hydrogen peroxide as oxidant. A "no-innocent" role of solvent, like ethyl acetate, is supposed and demonstrated for the epoxidation reaction with hydrogen peroxide as oxidant. As a matter of fact, the ethylacetate is reasonably hydrolyzed and form peracetic acid. Moreover, also other parameters have a strong influence on the epoxidation reaction.

It was found that the epoxidation system acetonitrile/alumina, barely reported in literature, is suitable for the efficient epoxidation of methyl oleate with hydrogen peroxide. Superior values of conversion and selectivity were found with acetonitrile, in comparison with the use of other solvents, demonstrating the strong influence of the solvent nature on the reaction rate. In order to reach high conversion and selectivity values, it is crucial to work with high oxidizing reactant/unsaturations molar ratios, with a careful control of the hydrogen peroxide feed rate, also considering the parallel decomposition reaction of hydrogen peroxide.

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