

Citral condensation with acetone on Na–MgO and Li–MgO catalysts

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Abstract

The effect of the Na and Li addition to MgO on the pseudo-ionone production from citral and acetone condensation in liquid phase is reported. The Na addition improves the yield to pseudo-ionone (defined as mol of produced pseudo-ionone/mol of converted citral), reaching a value of 100%, while the Li addition has a poor effect. These results can be related to the different distribution of basic sites. It was found that the catalytic activity depends on the acetone/citral and the catalyst/citral ratios. Besides, a poisoning effect of the reaction products on the catalysts was observed, even though the activity of the used catalysts can be partially restored by extraction treatments.

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1. Introduction

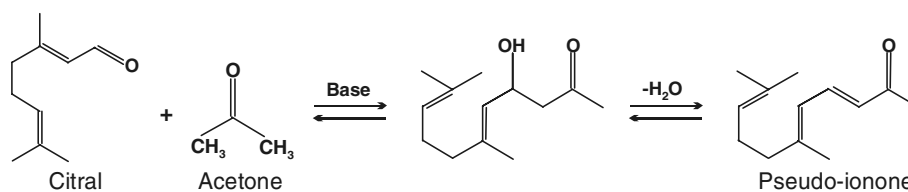
Pseudo-ionone is a very important product in fine chemistry, since it is an intermediary for the production of α and β -ionones, these two having a wide application both in medicine, like the synthesis of vitamin A from β -ionone [1,2], and perfumery [3]. Pseudo-ionone can be produced by citral and acetone condensation (Scheme 1) in an homogeneous phase by using alkali metal bases at low temperatures (313–323 K) and atmospheric pressure [4]. Under these conditions, a high selectivity can be reached. However, the use of the heterogeneous catalysis has many advantages since it facilitates the separation and purification of the products, mainly when a very high selectivity to the desired compounds is obtained. Hence, the development of solid catalysts with good activity, selectivity and stability could also reduce the production costs. It should be noted that there are not many data in the literature about this reaction by using heterogeneous catalysis mainly for alkali metal-doped

MgO. In fact, Climent et al. [5] found a good activity of pure MgO in the condensation of citral with acetone in liquid phase at 333 K, but the selectivity to pseudo-ionone was about 68%. Besides, Noda et al. [6] found good results using a CaO catalyst with a yield to pseudo-ionone close to 70%. The catalytic performance of hydrotalcite was higher than those of MgO and CaO, mainly when it was previously re-hydrated [7–9].

In this work, basic solid catalysts (MgO and MgO modified by Na or Li addition) were used for the production of pseudo-ionone from citral and acetone in liquid phase at atmospheric pressure. The objective of this work is related to the determination of the operating conditions to obtain the highest activity and selectivities to pseudo-ionones. Moreover, the effect of the addition of different amounts of Na or Li to MgO on the catalytic activity and selectivity was studied. With respect to the effect of the operating conditions, the incidence of the catalyst/citral weight ratio and the acetone/citral molar ratio on the catalytic performance was analyzed. The data in the literature about the effect of these operating conditions on the catalytic behavior is very scarce [10]. Besides, the problems associated with the

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Scheme 1. Citral and acetone reaction scheme [4].

catalyst deactivation by the reagent and/or products are also reported in this paper. The catalysts were characterized by measurements of the specific surface area (S_{BET}), X-ray diffraction, SEM, and TPD of pre-adsorbed CO_2 in order to explain the catalytic behavior.

2. Experimental

A very pure MgO (MgO powder from Alfa, Pura-tronic, 99.995% purity, $S_{\text{BET}} = 17 \text{ m}^2 \text{ g}^{-1}$) was used for the preparation of the catalysts. This sample was labeled as MgO.

In order to increase the surface area of MgO, two different treatments with deionized water ($10 \text{ ml H}_2\text{O g}^{-1}$ MgO) were carried out. The first one was performed at 373 K for 1 h [11], and the sample was labeled as MgO-S373, and the other one was performed at 298 K for 1 h (labeled as MgO-S). After these treatments, samples were filtered and then dried under vacuum at 373 K for 2 h. The alkali metal-doped catalysts were prepared by impregnation of MgO-S and MgO-S373 with an aqueous solution of NaOH (or LiOH) at 298 K by using a volume of impregnating solution/weight of support ratio of 7 ml g^{-1} . The Na and Li amounts in the impregnating solution were such as to obtain the desired loadings of each alkali metal. After the impregnations, the mixtures between MgO with the aqueous solutions of NaOH (or LiOH) were heated in open air at 353 K under stirring (600 rpm) until to obtain a paste, then it was dried at 393 K for 12 h and finally treated in flowing He at 1023 K for 3 h.

The S_{BET} measurements of the different samples were carried out in a Micromeritics ASAP 2000 equipment by using N_2 at 77 K. Before S_{BET} measurements, samples were treated at 473 K under high vacuum (10^{-4} torr) for 2 h.

The condensation of citral with acetone reaction was carried out at 323 K and atmospheric pressure in liquid phase under stirring (1400 rpm). The reaction took place in a reactor having two sections. The upper one was used for the thermal treatment of the catalysts (activation step). The reaction was performed in the section placed at the bottom of the reactor, which has also a cooling device to recover the acetone vapors released during the reaction. The two sections of this equipment are connected through a valve. The activation treatment

was carried out under vacuum (10^{-4} torr) at 693 K for 3 h. After this treatment, the sample was cooled down in situ up to 298 K, and then the catalyst was transferred to the reaction zone under vacuum (10^{-4} torr), by opening the valve. In this way, the contact of the catalysts with air is avoided. Then, He was introduced into the reactor to obtain a static He atmosphere (1 atm) and finally the mixture of citral and acetone (previously saturated with He) was injected. The acetone/citral molar ratio ($R_{\text{ACET/CIT}}$) used in the experiments ranged from 20 to 40 and the catalyst/citral weight ratio ($R_{\text{CAT/CIT}}$) varied from 0.4 to 0.68. Small amounts of liquid samples were withdrawn from the reactor at different times and analyzed in a GC-FID chromatographic system with a capillary column (Supelcowax 10 M \times 30 m).

In order to study the possible recovery of the catalytic activity after the reaction, the used catalysts were repeatedly washed with acetone under stirring (250 ml acetone g^{-1} ; 2, 4 or 6 times) for 30 or 60 min. After this treatment, the mixture catalyst-solvent was filtered under vacuum and then the solid was dried at 373 K for 12 h. The washed samples were activated in the same conditions as the fresh ones and then tested in the citral-acetone condensation reaction.

TPD measurements of pre-adsorbed CO_2 were carried out on samples (0.3 g) previously outgassed at 693 K under vacuum (10^{-4} torr) for 3 h and then cooled down to room temperature. The samples were immediately transferred to the TPD reactor and heated at 703 K under flowing He for 3 h. After the samples were cooled down to 298 K, a flowing CO_2 (100 ml min^{-1}) was passed through the catalyst bed for 2 h. After the CO_2 adsorption step, the samples were heated at 6 K min^{-1} from room temperature up to 720–783 K under flowing He (9 ml min^{-1}). The desorbed CO_2 amount released during the TPD was followed by using a TCD detector. CO_2 desorption profiles were deconvoluted in three peaks by using Lorentzian curves.

XRD determinations were performed in a Shimadzu diffractometer with a Cu $\text{K}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$), voltage: 30 kV and current 30 mA. Prior to the XRD measurements, samples were outgassed at 693 K and 10^{-4} torr for 3 h. Samples were stored in a dissicator in contact with dry air.

SEM microphotographies were obtained in a Microscope Jeol JSM-35C, operated at 20 kV. Samples were covered with a gold film before the analysis.

3. Results and discussion

XRD results (Table 1) for Li-doped MgO-S samples showed the characteristic lines of MgO, MgCO₃, Mg(OH)₂, Li₂O, LiOH, and Li₂CO₃ (the last one with a very low intensity). In the case of samples doped with Na, the following species were detected by XRD: MgO, Mg(OH)₂, MgCO₃, Na₂CO₃ and NaOH.

Fig. 1 shows the modification of the specific surface area for MgO after different treatments with water (S and S373) and doped with different Li contents. It can be observed that these treatments produce an important increase of the surface area of the MgO, this increment being slightly higher for the treatment at 298 K. Taking into account these results, it was selected the MgO-S sample to study the influence of the Na addition to MgO on the surface area. When increasing amounts of Li are added to MgO-S or MgO-S373, the specific surface areas decrease with respect to those of the undoped catalysts, this effect being more pronounced for Li-MgO-S373 samples (a decrease of 43% for 2 wt% Li with respect to the support was observed). Fig. 1 also shows the S_{BET} values for Na-doped MgO-S. It should be noted that when the Na amount increases, the S_{BET} values slightly decreases (7.5% with respect to the MgO-S

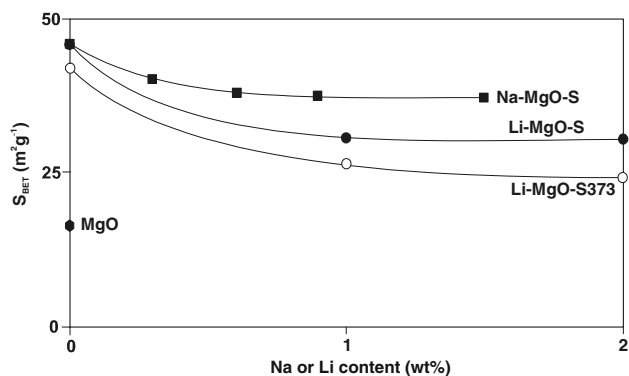


Fig. 1. Modification of the specific surface area for MgO-S, MgO-S373, and MgO-S and MgO-S373 doped with different amounts of Li and Na.

for 1.5 wt% Na). The different effects of Li and Na on the specific surface area can be related to the observations of SEM microphotographies, such as it will be discussed below.

Fig. 2 shows the effect of the different amount of the alkali metal added to MgO-S on the catalytic activity in citral condensation with acetone at $R_{\text{CAT}/\text{CIT}} = 0.4$ and $R_{\text{ACET}/\text{CIT}} = 25$. It should be noted that in all cases the selectivity of citral to pseudo-ionone, (defined

Table 1
XRD results

Species	Sample		Na 0.3 wt%		Na 0.9 wt%		Na 1.5 wt%		Na 1.5 wt%		Li 0.5 wt%		Li 1.0 wt%		Li 2.0 wt%		Li 2.0 wt%	
	MgO-S fresh		MgO-S fresh		MgO-S fresh		MgO-S fresh		MgO-S reaction		MgO-S fresh		MgO-S fresh		MgO-S fresh		MgO-S reaction	
	d (Å)	I_r	d (Å)	I_r	d (Å)	I_r	d (Å)	I_r	d (Å)	I_r	d (Å)	I_r	d (Å)	I_r	d (Å)	I_r	d (Å)	I_r
MgO	2.11	100	2.11	100	2.11	100	2.11	100	2.11	100	2.11	100	2.11	100	2.11	100	2.11	100
	1.49	66	1.49	66	1.49	66	1.49	66	1.49	66	1.49	66	1.49	66	1.49	66	1.49	66
	1.21	15	1.21	15	1.21	15	1.21	15	1.21	15	1.21	15	1.21	15	1.21	15	1.21	15
Mg(OH) ₂	4.77	3	4.77	3	4.77	3	4.77	3	4.77	3	4.77	3	4.77	3	4.77	3	4.77	3
	2.36	8	2.36	8	2.36	8	2.36	8	2.36	8	2.36	8	2.36	8	2.36	8	2.36	8
MgCO ₃	1.79	2	1.79	2	1.79	2	1.79	2	1.79	2	1.79	2	1.79	2	1.79	2	1.79	2
	2.74	3	2.74	3	2.74	3	2.74	3	2.74	3	2.74	3	2.74	3	2.74	3	2.74	3
	2.10	2	2.10	2	2.10	2	2.10	2	2.10	2	2.10	2	2.10	2	2.10	2	2.10	2
Na ₂ CO ₃	1.70	1	1.70	1	1.70	1	1.70	1	1.70	1	1.70	1	1.70	1	1.70	1	1.70	1
	–	–	2.97	<1	2.97	<1	2.97	<1	2.97	<1	–	–	–	–	–	–	–	–
	–	–	2.55	<1	2.55	<1	2.55	<1	2.55	<1	–	–	–	–	–	–	–	–
Na(OH)	–	–	2.37	<1	2.37	<1	2.37	<1	2.37	<1	–	–	–	–	–	–	–	–
	–	–	2.84	<1	2.84	1	2.84	2	2.84	2	–	–	–	–	–	–	–	–
	–	–	2.35	2	2.35	6	2.35	8	2.35	8	–	–	–	–	–	–	–	–
Li ₂ CO ₃	–	–	1.65	<1	1.65	1	1.65	2	1.65	2	–	–	–	–	–	–	–	–
	–	–	–	–	–	–	–	–	–	–	2.65	nd	2.65	<1	2.65	<1	2.65	<1
	–	–	–	–	–	–	–	–	–	–	1.88	nd	1.88	<1	1.88	<1	1.88	<1
Li(OH)	–	–	–	–	–	–	–	–	–	–	1.64	nd	1.64	<1	1.64	<1	1.64	<1
	–	–	–	–	–	–	–	–	–	–	4.35	nd	4.35	<1	4.35	<1	4.35	<1
	–	–	–	–	–	–	–	–	–	–	2.75	nd	2.75	<1	2.75	1	2.75	1
Li ₂ O	–	–	–	–	–	–	–	–	–	–	2.51	nd	2.51	<1	2.51	<1	2.51	<1
	–	–	–	–	–	–	–	–	–	–	2.66	nd	2.66	<1	2.66	1	2.66	1
	–	–	–	–	–	–	–	–	–	–	1.63	nd	1.63	<1	1.63	<1	1.63	<1
–	–	–	–	–	–	–	–	–	–	1.39	nd	1.39	<1	1.39	<1	1.39	<1	

d (Å): interplanar distance. I_r : ratio between the intensity of a given peak and the intensity of the maximum peak of MgO.

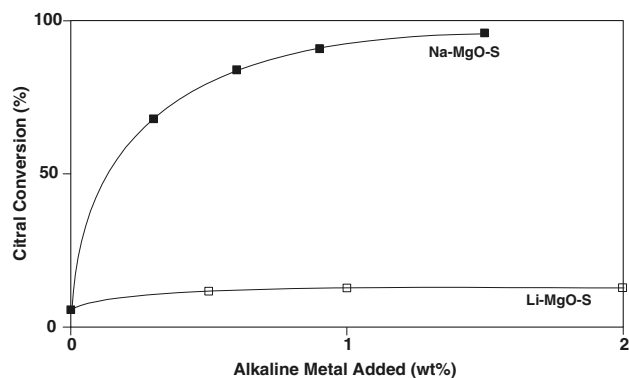


Fig. 2. Citral conversion as a function of the alkali metal content (Na and Li) added to MgO-S. Reaction time: 300 min. Reaction temperature: 323 K. $R_{ACET/CIT} = 25$ and $R_{CAT/CIT} = 0.4$.

as: mol of produced pseudo-ionone/mol of reacted citral), was 100%. Besides, other products, which are not involved in the citral consumption are also produced, like diacetonealcohol (derived from the acetone auto-condensation). It is observed that increasing amounts of Na added to MgO-S produce a very pronounced increase of the citral conversion (from 5.7% for MgO-S up to 96% for Na (1.5 wt%)-MgO-S), while the Li addition to MgO produces a smaller increase in the activity (from 5.7% for MgO-S up to 12.5% for Li (2 wt%)-MgO-S). This means a very important promoting effect of the Na addition to MgO-S on the catalytic activity. On the other hand, Li addition to MgO-S has a low promoting effect. From these results it was selected the Na (0.9 wt%)-MgO-S sample in order to analyze the effect of the operating conditions on the catalytic behavior.

The influence of the $R_{ACET/CIT}$ on the citral conversion was analyzed by performing 240 min experiments on Na (0.9 wt%)-MgO-S by using a $R_{CAT/CIT} = 0.4$. It was observed that the citral conversion increased from 85% up to 92% when the $R_{ACET/CIT}$ increases from 20 to 25, but for higher $R_{ACET/CIT}$ ratios (up to 40) the citral conversion remains practically constant. From these results, a $R_{ACET/CIT}$ molar ratio of 25 was adopted for testing all the catalysts.

In order to analyze the possible Na or Li leaching from the solid phase to the liquid one, due to the water formation during the reaction, a sample of spent catalyst and the corresponding liquid were taken after reaction and submitted to chemical analysis. Results showed that Li was undetectable in liquid phase, and a very small Na amounts was found in liquid phase (<0.01% referred to the original Na content for 1.5 wt% Na-MgO-S). This means a negligible leaching effect, and in consequence it can be inferred that the reaction is only catalyzed by the solid. Besides, after this treatment the solid was dried at 323 K and characterized by XRD. XRD results of samples after reaction did not show changes with respect to the fresh ones (see Table 1).

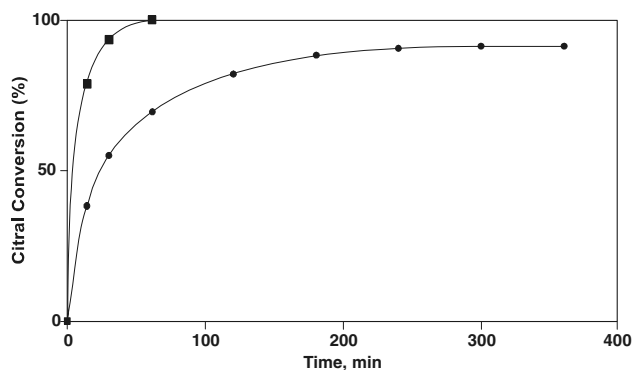


Fig. 3. Citral conversion as a function of the reaction time for different $R_{CAT/CIT}$ ratios: (●) 0.4 and (■) 0.68. Sample Na(0.9 wt%)-MgO-S. $R_{ACET/CIT} = 25$. Reaction temperature: 323 K.

Fig. 3 shows the effect of the $R_{CAT/CIT}$ on the citral conversion as a function of the reaction time for Na (0.9 wt%)-MgO-S. It is observed that the citral conversion increases when the $R_{CAT/CIT}$ increases, reaching 100% for $R_{CAT/CIT} = 0.68$ at 60 min of reaction time, while the citral conversion reaches a maximum value close to 92% for $R_{CAT/CIT} = 0.4$. It should be noted that the slope of the conversion-time curve for $R_{CAT/CIT} = 0.4$ at 300 min is close to zero, this meaning that the reaction is stopped at this time. This phenomenon, probably, can be related to the poisoning effect of the reaction products on the active sites of the catalysts. In order to check this hypothesis, an additional experiment was carried out by injecting the reaction products on a fresh sample of Na (0.9 wt%)-MgO-S, and after equilibration during 2 h, citral and acetone were injected to the reactor ($R_{CAT/CIT} = 0.68$, $R_{ACET/CIT} = 25$) at 323 K under stirring. The citral conversion under these conditions was only 7% at 1 h reaction time and it was kept constant for higher times. This means that the reaction products progressively poison the active centers of the fresh catalyst. It was mentioned that for $R_{CAT/CIT} = 0.68$, a total citral conversion and a total selectivity to pseudo-ionone can be reached on fresh samples. In this case, the concentration of the active sites of the catalysts is very high and in consequence, a fraction of active sites remains unpoisoned by the reaction products.

In order to analyze the possible recovery of the catalytic activity after reaction, several experiments were carried out by using spent catalysts and different washing conditions. Results showed that the maximum recovery of the catalytic activity was 47% by using 250 ml acetone g^{-1} and six washing steps for contact times higher than 30 min. After the extraction steps, only pseudo-ionone dissolved in acetone was detected. However, the strong adsorption of the other reaction products on the catalyst surface should not be discarded. Hence, it can be inferred that a fraction of

pseudo-ionone and other reaction products are irreversibly adsorbed on the catalyst after reaction and that the catalytic activity cannot be restored at the level of the fresh sample after this washing treatment. It should be noted that before the reaction on washed catalysts, samples were activated at 693 K and high vacuum, conditions at which water can be removed from the catalytic surface.

Fig. 4 shows the results of the desorbed CO_2 amounts (TPD) for MgO-S , Li-doped MgO-S and Na-doped MgO-S with different alkali metal contents. The TPD profile for MgO-S displays a low signal. When increasing amounts of Li are added to MgO-S , the TPD signals slightly increase. In the case of Na-doped samples, the TPD profiles are clearly larger than those of the Li-doped samples, and they increase as the Na content increases. From the deconvolution of the curves, it can be observed that MgO shows three CO_2 desorption peaks: the first one with a maximum at 379 K (LT), the second one is a very broad peak positioned at 523 K (MT), and the third one at 593 K (HT). It should be indicated that the literature also reports three CO_2 desorption peaks for MgO , Li– MgO and Na– MgO [12]. The temperatures of the CO_2 desorption peaks indicate the basic strengths

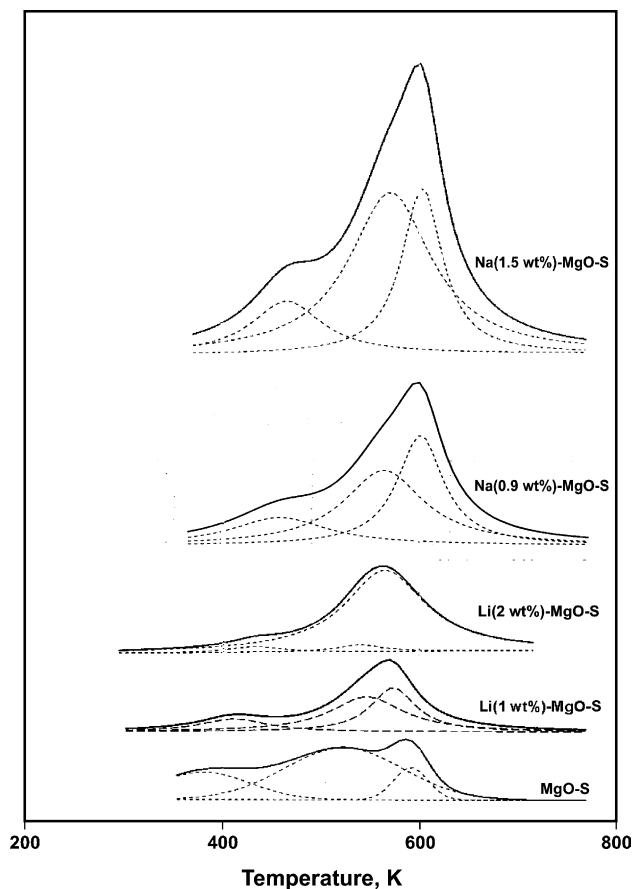


Fig. 4. TPD profiles of CO_2 for MgO-S , Li-doped MgO-S and Na-doped MgO-S samples.

of the sites, thus, the higher the desorption temperature, the higher the basic strength of the sites [13]. When Li is added to MgO-S , a modification of the distribution of the basic sites with different strength is observed. In fact, TPD profiles show that LT sites are very small, the MT ones decrease when the Li content increases and they are shifted to higher temperatures, and the HT peaks increase with the Li content, but they are shifted to lower temperatures with respect to MgO-S . Important differences in TPD profiles are observed for Na-doped MgO-S samples with respect to the other catalysts. Thus, the three types of sites show not only important increases in their magnitudes mainly MT and HT ones, but also they are shifted to higher temperatures. These results would indicate that the Na addition to MgO-S would produce a higher concentration of stronger basic groups than the Li– MgO-S . This behavior can be related to the different basicity between Li and Na. In fact, Diez et al. [12] reported that the higher basicity of Na/ MgO with respect to Li/ MgO could be attributed to a different electronegativity between both alkali metals. In conclusion, the different catalytic activity between Na– MgO-S and Li– MgO-S could be attributed to the different distribution and strength of the basic sites, mainly of the MT and HT ones.

Fig. 5 shows the SEM microphotographies of MgO-S and MgO-S doped with different Na and Li contents. These measurements were carried out on samples which were in contact with the atmosphere. It can be observed for MgO-S the typical structure of flakes, in agreement with other authors [14]. When increasing amounts of Li are added to MgO-S , the structure of flakes appears to be covered by layers of melted compounds, probably due to Li_2O , and in a minor proportion to Li_2CO_3 and LiOH , according to XRD results. It should be noted that the melting point of LiOH is 739 K and that of Li_2CO_3 is 891 K. It is reported in the literature that Mg ions of the MgO lattice can be exchanged by Li^+ to produce $[\text{Li}^+\text{O}^-]$ centers [15]. However, according to the catalytic results obtained in citral condensation, these centers appear to have a small activity for this reaction at low temperature in liquid phase. In the case of Na/ MgO-S samples, it can be observed that when increasing amounts of Na are added to MgO-S (Na^+ cannot be exchanged by Mg^{2+} ions of the MgO-S lattice due to Na^+ is larger than Mg^{2+}) the structure of flakes is retained, being progressively decorated, though partially, by small aggregates of Na compounds, probably $\text{Na}_2(\text{CO}_3)$ according to XRD results. These aggregates do not appear to show the picture of a melted structure, which is in agreement with the fact that the melting point of Na_2CO_3 (1164 K) is higher than the temperature used during the preparation (1023 K). However, it should be noted that the samples are activated at 693 K under high vacuum before reaction, and under this condition, the alkali metal carbonates can be

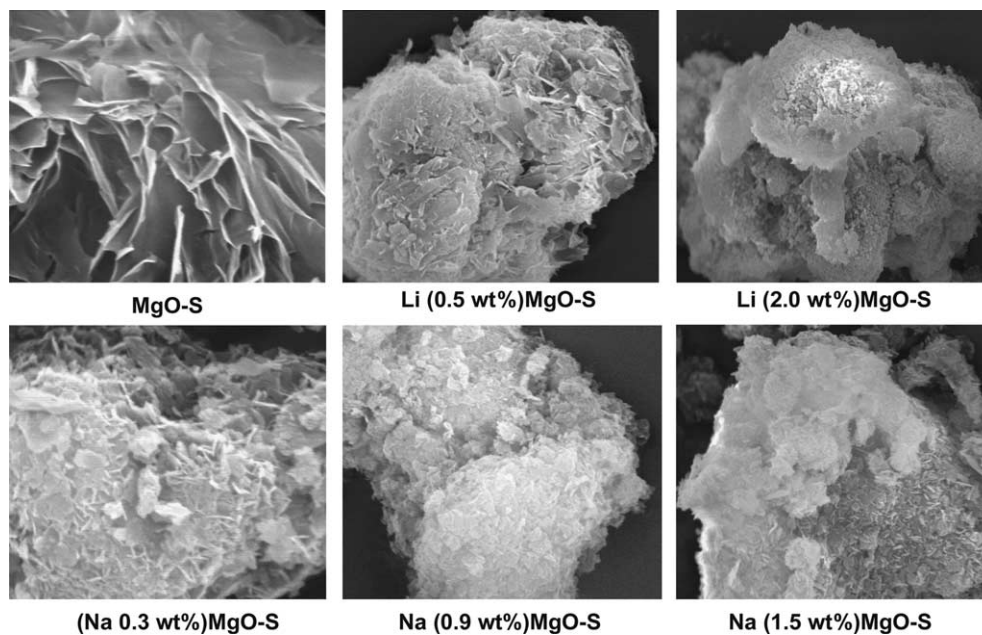


Fig. 5. SEM microphotographies of MgO-S, Li-doped MgO-S and Na-doped MgO-S samples.

decomposed releasing CO_2 (by thermodynamical reasons). In consequence, the active species at the beginning of the reaction appear to be the corresponding oxides.

It is worth noticing that the catalytic activity strongly depends on the pre-treatment of the sample. In fact, if the samples are in contact with traces of air before or during the reaction, the catalytic activity is negatively affected in an important way.

It must be remembered that Na-doped MgO-S samples show a small decrease of the surface area when increasing Na amounts are added to MgO-S. In the case of Li–MgO-S, the decrease of the surface area is clearly higher. These results are in agreement with the different coverage produced by the Li and Na addition on the structure of flakes of MgO (see SEM results).

4. Conclusion

The Na (>0.9 wt%) addition to MgO promotes the total transformation of citral into pseudo-ionones at $R_{\text{CAT/CIT}} = 0.68$ and $R_{\text{ACET/CIT}} = 25$. On the other hand, the Li addition to MgO has a very low effect on the yield to pseudo-ionone. The different catalytic behavior is related to a different distribution and strength of basic sites (according to TPD measurements) between the two catalyst series. In fact, Na-doped samples display a higher basicity and a higher basic strength than Li-doped ones. Besides, a poisoning effect of reac-

tion products on the active centers of the catalysts was also detected.

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