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How does γ-irradiation influence the phase transition of α-$NiMoO_4$?

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ABSTRACT

An attempt has been made to stabilize the high temperature β-$NiMoO_4$ phase which is catalytically more selective in oxidative dehydrogenation of alkanes at room temperature through irradiation by γ-rays. Different samples of stoichiomertic α-$NiMoO_4$ were subjected to different doses of γ-irradiation in the range of 50–500 kGy. The effect of γ-irradiation on the α- to β-$NiMoO_4$ transition temperature was studied using differential thermal analysis (DTA) technique with controlled rate of heating and cooling. The formation of β-$NiMoO_4$ phase was investigated by means of XRD and FT-IR techniques. The catalytic performance of the resulting catalyst samples in the oxidative dehydrogenation of cyclohexane at 500 °C was investigated. The DTA investigation revealed that γ-irradiation effectively lowers the temperature of the α → β transition in $NiMoO_4$ but did not affect the temperature of β-to-α return transition. A new peak characteristic of β-phase was detected at $2\theta = 26.3^\circ$ in the XRD patterns of γ-irradiated samples. FT-IR analysis also confirmed the formation of β-$NiMoO_4$ where a new band characteristic of β-phase was observed at 879 cm^{-1} in the spectra of these samples. In view of the XRD results, the observed change in the α- to β-$NiMoO_4$ transition temperature was attributed to the fact that radiation induced a strain in the α-$NiMoO_4$ crystals. On the other hand, catalytic activity results indicated that γ-irradiated nickel molybdate catalysts showed a high selectivity towards cyclohexene at isoconversion (5%) in comparison with that of unirradiated parent α-$NiMoO_4$.

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1. Introduction

Nickel molybdates are important catalysts for the partial oxidation of hydrocarbons and precursors in the synthesis of catalysts for hydrotreatment of oil fractions [1,2]. The β-phase of $NiMoO_4$ is more selective for the oxidative dehydrogenation (ODH) of alkanes to alkenes than α-phase [3,4]. However, β-phase is not stable at room temperature and a temperature of ca. 700 °C is needed for obtaining full transformation of α → β-phase. Different groups of investigators have done several trials to stabilize β-$NiMoO_4$ phase at room temperature [5,6].

It has been reported that γ-irradiation produced important modifications in catalytic and structural properties of various metal oxides based on Ni, Co and Mo [7–10]. In the present work, an attempt has been made to enhance α → β transition in the $NiMoO_4$ at room temperature by applying different doses of γ-rays. The irradiated solid samples were tested in ODH of cyclohexane as a model reaction, with hope to detect any change or tendency in their catalytic performances. The effect of γ-irradiation on the transition temperature of α- to β-phase was investigated by differential thermal analysis (DTA). The phase composition of the irradiated catalyst samples was analyzed by X-ray diffraction (XRD) and the change in molecular structure was investigated by both FT-IR and Raman spectroscopy.

2. Experimental

2.1. Materials

Pure stoichiometric α-$NiMoO_4$ was prepared by coprecipitation from aqueous solutions of 750 ml of 0.057 M ammonium heptamolybdate (Merck +99%) and 750 ml of 0.4 M of nickel nitrate (Aldrich +99%) in the thermo-regulated conditions at temperature of 63 °C and at pH 6.0 [11,12]. After drying of precursor at 110 °C, solid was calcined at 550 °C. The prepared nickel molybdate showed that a diffraction pattern corresponds to α-$NiMoO_4$ phase (JCPDS File Card No. 33-0948) [13].

Different samples of α-$NiMoO_4$ in Gamma cell 220 Excel were subjected to different doses of γ-radiation (50, 100, 200, 350 and 500 kGy) using ^{60}Co irradiation facility (manufactured by MDS Nordion, Canada), with activity of 11994.8 Ci at the time of installation (18 January 2002) and absorbed dose rate is in the range 7.845–7.666 $kGy\,h^{-1}$ over the time of the whole work. The overall uncertainty of the absorbed dose rate is ±2.4% at the 95% confi-

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dence level. Solid samples were left two weeks before DTA, XRD and FT-IR analysis. No special temperature control was attempted, but irradiation temperatures were probably not above 100 °C.

2.2. Apparatus and techniques

Differential thermal analysis (DTA) of unirradiated and γ-irradiated α-$NiMoO_4$ samples was performed using Shimadzu-50 and DTA-50-autosphere thermal analyzer with differential scanning calorimeter cell. A 3–5 mg sample of each solid was used in each test. Analysis conditions were: heating rate 10 °C/min, cooling rate 10 °C/min, maximum temperature 900 °C.

XRD diffraction patterns were recorded on a Shimadzu diffractometer XD-D1 X-ray diffraction spectrometer with a Cu target ($\lambda = 1.5406$ Å) for 2θ angles varying from 10° to 80° and an operating voltage of 40 kV and an electric current of 30 mA. The crystal size (t (Å)) of α-$NiMoO_4$ was calculated by using the Scherrer formula: t (Å) = $0.92\lambda/(B\cos\theta)$, where B is the width at the half maximum of the 220 reflection line. The strain (e) was evaluated by using the Langford single line formula [14]: $e = B_g/(4\tan\theta)$, where B_g is the integral width of the Gauss profile of 220 reflection line.

FT-IR measurements were performed by using Thermo-scientific, Nicolet 6700 at a resolution 5.3 cm^{-1} over the wave 40,000–400 cm^{-1}.

Laser Raman spectroscopy was performed with a Dilor Labram spectrometer. Further details can be found elsewhere [6].

2.3. Catalytic test

Catalytic activity measurements were performed employing a conventional fixed-bed reactor system using air as the carrier gas for the cyclohexane feed. The following reaction conditions were employed: catalyst weight, 0.2 g; flow rate of air, 20 ml/min; molar

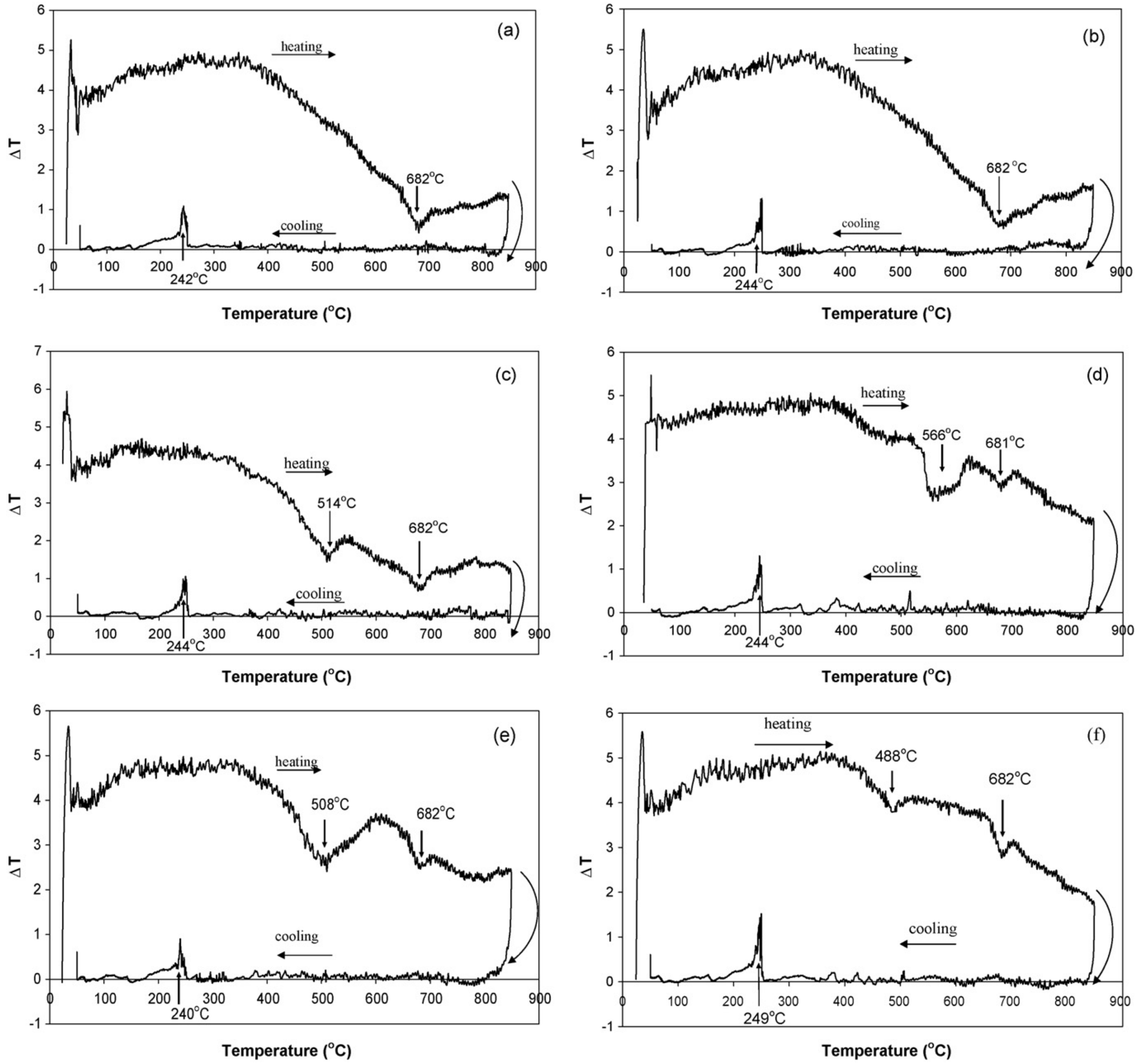

Fig. 1. DTA heating and cooling curves of unirradiated and irradiated α-$NiMoO_4$ samples by different doses of γ-ray: (a) unirradiated, (b) 50 kGy, (c) 100 kGy, (d) 200 kGy, (e) 350 kGy and (f) 500 kGy.

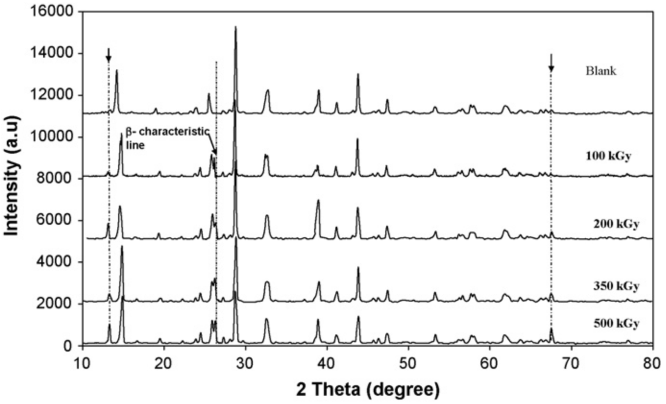

Fig. 2. XRD patterns of pure α-$NiMoO_4$ and irradiated samples by different doses of γ-ray (100–500 kGy).

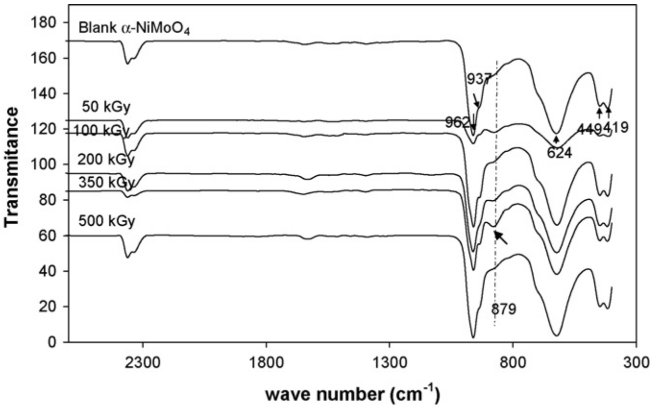

Fig. 3. FT-IR spectra of pure α-$NiMoO_4$ and irradiated samples by different doses of γ-ray (50–500 kGy).

feed rate of cyclohexane, 4×10^{-3} mol/h; reaction temperature, 500 °C. To make a comparison between selectivity of different catalysts; cyclohexane conversion was adjusted at conversion level of 5% [6]. Analysis of reactants and products was performed by an on-line Shimadzu GC-17A with FID and TCD detectors using two columns; fused silica FFAP-capillary (50 m × 0.32 m i.d., AD: 0.46) (for cyclohexane, cyclohexene, cyclohexadiene and benzene) and HaySep D (80/100) (for CO_x). No homogeneous gas phase reaction for conversion of cyclohexane was observed at this temperature.

3. Results and discussion

Fig. 1 displays the DTA thermograms of unirradiated and γ-irradiated α-$NiMoO_4$ samples. The DTA cycle of phase transition in the stoichiometric α-$NiMoO_4$ system showed a strong endothermic peak with its maximum at ca. 682 °C; this peak can be attributed to the α → β transition in the $NiMoO_4$ [15,16]. On the other hand, the exothermic peak detected during cooling at ca. 242 °C corresponds to β → α transition.

No significant change was observed in the thermogram (Fig. 1b) of the sample irradiated with 50 kGy dose in comparison with that of pure α-$NiMoO_4$. The thermograms (Fig. 1c–f) of γ-irradiated α-$NiMoO_4$ samples by doses in the range of 100–500 kGy showed that the same endothermic peak corresponds to α-to-β transition with its maximum at ca. 682 °C in all cases. However, a new endothermic peak was detected at lower temperature in the thermograms of these samples and the position of this peak shifted to lower temperature with increasing the γ-rays dose (Fig. 1c–f). On the other hand, the location of the exothermic peak corresponding to β-to-α reverse transition remained unchanged in comparison with that of unirradiated α-$NiMoO_4$ sample.

Fig. 2 demonstrates a comparison between XRD pattern of the parent nickel molybdate and that of samples irradiated by different doses of γ-rays. Radiation of α-$NiMoO_4$ samples with 50 kGy γ-rays dose did not result in observable changes in the X-ray powder diffraction pattern of this sample. However, in the case of the samples irradiated by doses in the range of 100–500 kGy, a strong peak was detected at $2\theta = 26.3^\circ$ of d-spacing 3.38 Å which is possibly referred to the principle line of the β-$NiMoO_4$ [17]. In addition, two new weak peaks were also detected at $2\theta = 13.2$ and 67.8° of d-spacing 6.70 and 1.38 Å, respectively. These peaks are also characteristic of β-phase $NiMoO_4$ (JCPDS File Card No. 12-0348) [13]. Furthermore, the position of the peaks in the range of $2\theta = 10–25^\circ$ shifted to higher degree.

The IR spectra of unirradiated and γ-irradiated α-$NiMoO_4$ samples are shown in Fig. 3. The obtained IR spectrum of unirradiated α-$NiMoO_4$ is very similar to that reported in Refs. [3,18], which is characterized by bands at 937 and 962 cm^{-1}. The spectra of γ-irradiated samples showed the main characteristic peaks of the parent α-$NiMoO_4$. In addition, a new absorption band was detected at 879 cm^{-1}. This band can be attributed to stretching vibrations of Ni–O–Mo in the tetrahedral coordination of β-$NiMoO_4$ [3,5]. It is noticeable that, this band is more pronounced in the spectrum of the sample irradiated by 350 kGy dose. These FT-IR results run in good harmony with the obtained XRD results and can confirm the partial stabilization of β-$NiMoO_4$ in the γ-irradiated samples at room temperature.

Fig. 4 showed the Raman spectra of the parent α-$NiMoO_4$, γ-irradiated α-$NiMoO_4$ by 350 kGy collected at room temperature and that of the same irradiated sample collected at 600 °C during heating for 2 h in air. The spectrum of α-$NiMoO_4$ (Fig. 4a) consisted of a very strong peak at 961 cm^{-1} and two strong peaks at 912 and 707 cm^{-1}. This spectrum is consistent with that reported for stoichiometric α-$NiMoO_4$ in Ref. [11]. The spectrum (Fig. 4b) of the irradiated sample collected at room temperature clearly presents bands due to α-$NiMoO_4$. In addition, new bands were detected at 943, 895 and 822 cm^{-1}. These new bands can be assigned to the β-$NiMoO_4$ phase [19]. On the other hand, the very strong characteristic bands of MoO_3 at 996, 817 and 667 cm^{-1} are not observed [11]. These results indicate that by irradiation of α-$NiMoO_4$ the well-defined spectrum obtained is unambiguously described by a mixture of α- and β-phase $NiMoO_4$. As shown in Fig. 4c, heating

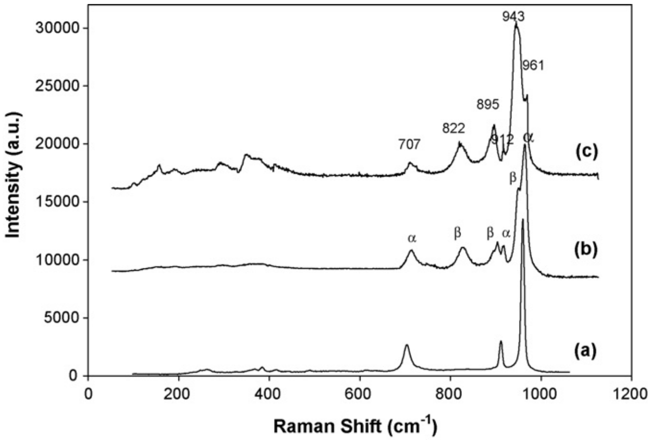

Fig. 4. Raman spectra of α-$NiMoO_4$ (a) parent sample collected at room temperature, (b) γ-irradiated sample by 350 kGy collected at room temperature and γ-irradiated sample by 350 kGy collected during heating for 2 h in air at 600 °C.

Table 1
Calculated strain (e), particle size (t) and mole fraction of β-phase (X_β) of unirradiated α-$NiMoO_4$ and irradiated samples by different γ-ray doses

Radiation dose (kGy)	$e \times 10^3$	t (Å)	$X_\beta = I_{3.38}/I_{3.09}$
0 (pure)	2.95	483.0	0.00
100	3.09	462.3	0.22
200	3.20	445.0	0.23
350	3.35	424.7	0.38
500	3.80	375.0	0.45

X_β is the molar fraction of β-phase in the irradiated sample, equal to ratio between the integrated intensity of the principle line of the β-phase of d-spacing 3.38 Å and the integrated intensity of the principle line of α-phase of d-spacing 3.09 Å.

γ-irradiated α-$NiMoO_4$ sample at 600 °C for 2 h in air produced a decrease in the intensity of the bands characteristic of α-$NiMoO_4$. This decrease accompanied by an increase in intensity of the bands characteristic of the β-$NiMoO_4$. Cooling the sample back to room temperature restored the Raman features present in the spectrum of γ-irradiated α-$NiMoO_4$ sample prior to heating.

The new endothermic DTA peak observed in the thermograms of γ-irradiated samples can be attributed to one of the following possibilities: (i) decomposition of α-$NiMoO_4$ to oxides, for example, NiO, MoO_3; (ii) transfer some of α-$NiMoO_4$ molecules to β-phase at lower temperature. XRD, FT-IR and Raman data obtained in the present work exclude the possibility of decomposition of α-$NiMoO_4$ to oxides, where neither the peaks nor the bands characteristic of these oxides are observed. It has been reported that [14,20,21] γ-irradiation produced a strain in metal oxides and that consequently induced some kind of lattice damage. Furthermore, the lattice damage induced by γ-irradiation involved creation of vacancies and interstitial atoms and that have a positive effect on the phase transformation of the metal oxides [22,23]. The XRD results in Table 1 showed that γ-irradiation increased the strain (e) in the α-$NiMoO_4$ crystals and this was accompanied by a decrease in the particle size (t). Moreover, it is clear that the value of the strain increased with increasing radiation dose. According to these XRD results it seems that γ-irradiation of α-$NiMoO_4$ increased strain in its crystals and exerted positive effect on the α- to β-phase transition. Thus, the new peak observed in the thermograms of irradiated samples can be attributed to easier α → β transition in irradiated $NiMoO_4$ at lower temperature than that of unirradiated parent α-$NiMoO_4$ sample. In other words, γ-irradiation increased strain in α-$NiMoO_4$ crystals and consequently the principal peak corresponds to α → β transition splitted in two at lower temperature which facilitated the formation of stable β-$NiMoO_4$ phase at room temperature.

The data of the new endothermic peak indicating the α → β transition in irradiated $NiMoO_4$ samples are listed in Table 2. Since approximately constant weight of solids was taken in each run, the integrated area of the endothermic peak for each solid could be regarded as a measure of the amount of β-$NiMoO_4$ formed. It can be seen from Table 2 that the transition temperature decreased progressively with increasing radiation dose; except in the case of the sample irradiated with a 200 kGy dose. These results suggest that increasing the radiation dose enhanced α- to β-phase transition. On the other hand, the area of this peak attained a maximum value at radiation dose 350 kGy (Table 2); increasing radiation dose to 500 kGy produced a significant decrease in the area ca. 77%.

Table 2
Effect of γ-radiation dose on the transition temperature and integrated area of the new endothermic peak of the DTA curves of irradiated α-$NiMoO_4$

Radiation dose (kGy)	Temperature (°C)	Peak area (a.u.)
100	514	42.0
200	566	103.9
350	508	154.3
500	488	36.0

Table 3
Catalytic results in cyclohexane ODH over unirradiated and irradiated α-$NiMoO_4$

Radiation dose (kGy)	S (C_6H_6)[a] (%)	S (C_6H_{10})[b] (%)	S (C_6H_8)[c] (%)	S (CO)[d] (%)	S (CO_2)[e] (%)
0 (pure)	71	24.0	0.2	0.7	4.1
50	68.1	25.8	0.9	1.1	4.1
100	58.6	33.8	1.8	2.6	3.2
200	55.4	36.8	2.7	2.6	2.5
350	51.8	39.2	3.5	3.1	2.4
500	53.1	38.6	3.4	1.6	3.3

Cyclohexane molar feed rate: 4×10^{-3} mol/h g, W = 0.2 g and temperature 500 °C.

[a] Selectivity to benzene at conversion level of 5%.

[b] Selectivity to cyclohexene at conversion level of 5%.

[c] Selectivity to cyclohexadiene at conversion level of 5%.

[d] Selectivity to CO at conversion level of 5%.

[e] Selectivity to CO_2 at conversion level of 5%.

It can be concluded that increasing radiation dose from 350 to 500 kGy led to a decrease in the thermal stability of the formed β-$NiMoO_4$ and this probably is due to partial decomposition of β-$NiMoO_4$ to amorphous oxides (viz., NiO, MoO_3). This might be due to the fact that β-phase of $NiMoO_4$ is ~9 kcal/mol less stable than the α-phase [24]. It seems that these oxides are amorphous and their concentrations are too small to be detected by XRD. These trends in the stability of the formed β-phase agree well with the obtained XRD and FT-IR results, where the intensity of XRD peak at $2\theta = 26.3^\circ$ and that of the IR band at 879 cm^{-1} characteristic of β-phase increased with increasing radiation dose to 350 kGy then decreased when using 500 kGy.

The calculated selectivities of the reaction products at isoconversion (5%) for all the studied catalysts are listed in Table 3. The oxidation of cyclohexane over all the catalysts under study yielded cyclohexene, 1,3-cyclohexadiene and benzene as organic products as well as CO_2 and CO as inorganic carbon products. It is clear from Table 3 that unirradiated α-$NiMoO_4$ is the most selective to benzene among all studied catalysts. It is also note worthy that irradiated catalysts sample are more selective to benzene than partial ODH products; cyclohexene and cyclohexadiene. However, these irradiated catalysts have a higher cyclohexene and cyclohexadiene selectivities than that of the unirradiated parent α-$NiMoO_4$. Moreover, the results in Table 3, revealed that the selectivity of the γ-irradiated catalysts to the partial ODH products is dependent on the dose employed; where the selectivity to the partial ODH products attained a maximum value at 350 kGy, then dropped by increasing radiation dose from 350 to 500 kGy.

The above catalytic results show that α-$NiMoO_4$ catalysts irradiated by γ-rays of different doses in the range (100–500 kGy) exhibited higher selectivity to cyclohexene than parent α-$NiMoO_4$. Mazzochia et al., reported that β-$NiMoO_4$ is more selective in ODH of propane to propene and β/α ratio in the $NiMoO_4$ catalyst directly influence on the propene selectivity [25]. In the present work, β-$NiMoO_4$ was detected together with α-phase by XRD, FT-IR and Raman (Figs. 2–4) in the irradiated catalysts. In addition, it was observed that, the β/α ratio in the $NiMoO_4$ increased with increasing γ-radiation dose (Table 1). This suggests that oxidative dehydrogenation of cyclohexane to cyclohexene over these irradiated catalysts is mainly affected by the β/α ratio in the $NiMoO_4$ (Table 1). It is remarkable that the β-phase was not detected in the α-$NiMoO_4$ catalyst irradiated by 50 kGy dose and this well correlated with lower selectivity of this catalyst towards cyclohexene. The above interpretation suggests that the created β-phase in the $NiMoO_4$ plays a decisive role in determining the selectivity of irradiated catalysts towards cyclohexene.

On the other hand, when comparing the CO_x (CO and CO_2) selectivity over the unirradiated and irradiated catalysts (Table 3), it seems that the CO_x selectivity almost constant for all catalysts. However, it is clear that unirradiated α-$NiMoO_4$ and irradiated catalyst with 50 kGy dose are the most selective to CO_2 as a total oxidation undesired product of cyclohexane. As can be also seen in Table 3, γ-irradiated catalysts by doses in the range of 100–500 kGy are more selective to CO than parent α-$NiMoO_4$. These results suggest that irradiation of α-$NiMoO_4$ by γ-rays decreased its total oxidation character. These observed modifications in the CO and CO_2 selectivities can also be related to the creation of β-phase in the irradiated catalysts [26].

Finally, it seems that 350 kGy is the optimum radiation dose to enhance α-$NiMoO_4$ selectivity in partial ODH of cyclohexane for the following reasons: (i) the irradiated catalyst by 350 kGy dose has approximately the same cyclohexene selectivity as the catalyst irradiated by 500 kGy dose, (ii) the same catalyst has a lower CO_2 selectivity than that one exposed to 500 kGy dose. According to the DTA results in Table 2, the higher CO_2 selectivity achieved with catalyst irradiated by 500 kGy in comparison with catalyst irritated by 350 kGy is probably due to decomposition of the selective β-phase to oxides (viz., NiO, MoO_3). In fact, it is well known that these oxides favour oxidation of hydrocarbons to CO_2 [27].

4. Conclusions

In the present study, the effect of γ-irradiation on the $\alpha \rightarrow \beta$ phase transition in the $NiMoO_4$ and on catalytic performance of α-$NiMoO_4$ in oxidative dehydrogenation of cyclohexane was investigated. The salient findings are described below.

First, γ-irradiation lowered the temperature of the α- to β-$NiMoO_4$ phase transition. This effect was attributed to the fact that irradiation induced a strain in α-$NiMoO_4$ crystals.

A second important point is that irradiated catalysts by γ-rays doses in the range (100–350 kGy) are more selective to partial ODH products; cyclohexene and cyclohexadiene. The higher selectivity to cyclohexene and cyclohexadiene of irradiated catalysts could be connected with the partial stabilization of the more selective high temperature phase β in these samples at room temperature.

The third aspect is that the degree of stabilization of β-$NiMoO_4$ depending on the radiation dose. Further investigations are necessary to precisely determine the optimum radiation dose to transfer large number of α-$NiMoO_4$ molecules to the mentioned above phase.

The final remark is that these results could have an industrial interest because it avoids heating of the reactor at high temperature ca. 700 °C to maintain catalyst in β-configuration.

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