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High yield hydrogen from the pyrolysis-catalytic gasification of waste tyres with a nickel/dolomite catalyst

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Abstract:

Nickel/dolomite catalysts have been prepared and investigated for their suitability for the production of hydrogen from the two-stage pyrolysis–gasification of waste tyres. Experiments were conducted at a pyrolysis temperature of 500 ^{o}C and gasification temperature was kept constant at 800 ^{o}C with a catalyst/ waste tyres ratio of 0.5. Fresh and reacted catalysts were characterized using a variety of methods, including, BET, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM)-energy dispersive X-ray spectrometry (EDXS). The results indicated that the gas yield was significantly increased from 30.3 to 49.1 wt.% and the potential H_2 production was doubled with the introduction of 5%Ni into the calcined dolomite catalyst. The results show also a further increase in the gas yield and the potential H_2 production with increasing Ni loading from 5 to 20 wt.%. The coke deposited on the catalyst surface was 3.2, 6.1, 7.9 and 10.1 wt.%, when the Ni loading was 0, 5, 10 and 20 wt.% for the calcined dolomite catalyst, respectively. The results showed that the calcined Ni dolomite catalysts became deactivated by filamentous carbons.

Keywords: Hydrogen; Catalyst; Pyrolysis; Gasification; Tyre; Waste

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1 Introduction

There is much concern about the shortage of fossil fuels as well as the global warming impact associated with the use of these fuels. Hydrogen is considered as a clean energy resources for the future. At present about 5×10^{11}Nm^3 of hydrogen is produced each year in the world and mainly produced from fossil fuel sources (about 96%) using different techniques such as methane steam reforming, oil reforming and coal gasification [1].

The rapid increase in cars and trucks leads to huge amounts of waste tyres being produced every year around the world. It has been reported that about 3.4 million tonnes of waste tyres are generated in Europe [2] and about 5 million tonnes in the U.S [3] each year. Different methods have been used to deal with waste tyres such as material recovery, energy recovery and retreading. Steam gasification of waste tyres seems to be a promising process for hydrogen production [4-6].

The catalytic steam gasification of biomass and waste have been studied by using different metals based catalysts and supports [7,8]. Noble metals such as Pt, Pd, Rh and Ru are found to be very effective for hydrogen production [9,10] but they are not used as a bulk industrial catalyst because of their high cost. Nickel based catalysts have been found to be very active catalysts for hydrogen production. However, Ni catalysts tend to be deactivated due to carbon deposition and sulfur poisoning [11,12]. Therefore, many researchers have carried out experiments to improve the properties of the Ni catalysts. Furthermore, waste tyres contain sulfur at levels of about 1.0 wt% in the form of organo-sulfur compounds [13] and the gas produced from the pyrolysis of waste tyres contains mainly hydrogen sulphide in high concentration [14]. Therefore, the catalyst, which is used in catalytic steam gasification of waste tyres, should have a high resistance to sulfur poisoning. Ni/dolomite catalysts are one of the most promising catalysts in terms of tar reduction with reported excellent catalytic activity [15,16]. Furthermore, Ni/dolomite catalysts showed excellent resistance to coking and sulfur poisoning and they are relatively inexpensive compared with other catalysts [17].

In this paper, catalysts in the form of calcined dolomite and the influence of nickel content were investigated to determine their effect on hydrogen production from the steam pyrolysis-gasification of waste tyres.

2 Experimental Methods

Shredded used passenger car tyres (approximately 6 mm particle size) were employed for this study. The Ni/dolomite catalysts were prepared by precipitating metallic nickel onto calcined dolomite. Nickel nitrate hexahydrate was dissolved into distilled water before the addition of dolomite which had been calcined at 1000 ^{o}C for 3 h. the catalyst was filtered and washed with hot water. The catalyst was dried at 105 ^{o}C overnight followed by calcination in air at 500 ^{o}C for 3 h. Ni loadings of 5, 10 and 20 wt.% were investigated in this work. The dolomite, crushed and sieved to the same size as the catalyst before calcination, originated from the Warmsworth quarry in Northern England, UK. Its composition was 21.3 wt% MgO, 30.7 wt% CaO, 0.3 wt% SiO_2, 0.27 wt% Fe_2O_3, and 0.1 wt% Al_2O_3.

2.1. Experimental system

The catalytic pyrolysis-gasification of waste tyre was carried out using a two stage fixed bed reactor. A schematic diagram of the reactor system is shown in Fig. 1. The tyre sample was pyrolysed in the first stage at 500 °C and then the pyrolysis products were passed directly to a second stage where steam catalytic gasification of the pyrolysis products was carried out. The details of the experimental procedure and reactor system are presented in our previous work [4].

Approximately 1.0 g of tyre sample was held in the first stage and 0.5 g of catalyst was held in the second stage. In these experiments, the gasification temperature was 800 °C and the steam flow rate was 4.74g h^{-1}. The evolved products from the reaction system passed through an air-cooled condenser and two dry ice cooled condensers where liquid products were collected. The non-condensable gases were analysed off-line by gas chromatography using two detectors: a thermal conductivity detector (TCD) and a flame ionization detector (FID). Nitrogen, hydrogen, oxygen, and carbon monoxide were analysed by the TCD detector whilst the hydrocarbon components from C_1 to C_4 were detected by the FID.

2.2. Catalyst characterization

The specific surface area of the fresh catalysts was measured by the BET method with N_2. The BET surface area and composition of the prepared catalysts are shown in Table 1. XRD patterns of all Ni/Dolomite catalysts calcined at various calcinations temperatures were analyzed by a Philips PW 1050 Goniometer using a PW1730 with a CuKa radiation X-ray tube. The temperature-programmed oxidation (TPO) of dolomite and reacted Ni/dolomite catalysts was carried out using a Stanton-Redcroft thermogravimetric analyser (TGA). The fresh and reacted catalysts were characterized by scanning electron microscope (SEM) (LEO 1530) coupled to an energy dispersive X-ray spectrometer (EDXS).

3 Results and discussion

3.1. Characterization of nickel/dolomite catalyst

Table 1 shows the surface areas for the catalysts produced for the investigation of hydrogen production from gasification of waste tyres. The data shown in Table 1 indicates that the BET surface area increased slightly from 32.6 to 38.2 m^2 g^{-1} when Ni loading on the calcined dolomite catalyst increased from 5 to 10 wt.%. However, the BET surface area reduced to 31.8 m^2 g^{-1} with a further increase of Ni loading to 20 wt.%. 10%Ni/dolomite catalyst produced by a precipitating process at the calcination temperature of 500 ^oC for steam gasification of toluene and naphthalene was investigated by Srinakruang et al. [18]. The BET surface area of the produced catalyst was found to be 27.0 m^2g^{-1}. A 11.06 wt.% Ni/dolomite catalyst was prepared by Chaiprasert and Vitidsant [19] for the steam reforming of coconut shell. The BET surface area of the prepared catalyst was reported to be 29.22 m^2 g^{-1}. These results are similar to the 10%Ni/dolomite catalyst which prepared in this paper.

Fig. 2 shows the scanning electron micrographs (SEM) and energy dispersive X-ray spectrograms (EDXS) for fresh dolomite, fresh calcined dolomite catalyst and fresh 10%Ni/dolomite catalyst. As shown in Fig. 2, the dolomite has fine fluffy dolomite particles sticking to the dolomite crystals. After the calcination process to 1000 ^oC, the amount of this material was largely increased due to the breakdown of larger grains to small fines (Fig. 2). Fig. 2 also suggests that the porosity was increased for the 10%Ni/dolomite catalyst compared with calcined dolomite catalyst.

The TGA-TPO and DTG-TPO results of fresh dolomite are presented in Fig. 3. The DTG-TPO result shows two peaks were observed. It is suggested that these peaks might be assigned to the thermal decomposition of dolomite to CaO and MgO phases which is confirmed also by XRD analysis (Fig. 4). The TGA-TPO result shows that the thermal decomposition of dolomite is completed at about 900 ^oC. Gunasekaran et al. [20] also reported that the two peaks observed in the thermal decomposition of dolomite was caused by decarbonation of magnesium carbonate and calcite and that the thermal decomposition was completed at about 950 ^{o}C when the thermal decomposition behaviour of dolomite was investigated by thermogravimetric (TG) analyser.

X-ray diffraction analysis was carried on the fresh dolomite, calcined dolomite and 10%Ni/dolomite catalysts and the results are presented in Fig. 4. Fig. 4 shows the presence of only CaO and MgO phases in calcined dolomite, confirming the complete decomposition of dolomite which was obtained by The TGA-TPO result (Fig. 3). Fig. 4 shows also the presence of spinel phase ($NiMgO_2$), NiO, CaO and MgO in the 10%Ni/dolomite catalyst. A 10%Ni/dolomite catalyst calcined at 500, 750 and 950 ^{o}C was investigated by Srinakruang et al. [18] using XRD analysis. They found that The $NiMgO_2$ phase was present in all the Ni/Dolomite catalysts calcined at various temperatures, whereas the NiO phase was present for the catalyst calcined at 500 ^{o}C only. It was found that stronger interaction between Ni and the catalyst support, which results in the formation of stable Ni species ($NiMgO_2$ phase), increased the dispersion of Ni and retarded the sintering of Ni during the reforming process. They found also that the highly dispersed Ni improved the reforming activity and the resistance of coke deposition [21].

3.2. Calcined Dolomite and Ni/Dolomite catalyst

Dolomite catalyst has been extensively employed in steam gasification processes to improve the yield and quality of product gas and to reduce tar yield using different feed stocks such as biomass [16,22] and waste [23,24]. However, there few data have been found on the use of dolomite catalyst in the steam gasification of waste tyres. In this work, calcined dolomite and 5%Ni/dolomite catalysts were investigated for their influence on the pyrolysis-gasification of waste tyres. The product yield from the experiments with calcined dolomite and 5%Ni/dolomite are shown in Table 2. The product gas, oil, and solid were calculated in relation to the mass of waste tyres only, therefore resulting in more than 100% mass balance, since the added water will influence the gas production and therefore the mass balance. The data shown in Table 2 indicates that the gas yield was largely increased from 30.3 to 49.1 wt.% and the reacted water was increased from 0.12 to 021 g with the introduction of 5%Ni into the calcined dolomite catalyst. However, the oil yield in relation to the mass of waste tyre only shows a small reduction with the 5%/dolomite catalyst compared to the calcined dolomite catalyst.

The concentration of gas produced with calcined dolomite and 5%Ni/dolomite catalyst in the catalytic steam pyrolysis–gasification of waste tyres is shown in Fig. 5. The results indicate that the H_2 concentration was increased from 49.1 to 55.0 vol.%, CO concentration was increased from 5.2 to 7.7 vol.% and there was a large decrease in methane concentration from 21.2 to 14.0 vol.% and CO_2 decreased from 15.7 to 13.5 vol.%, by introducing 5wt.% of Ni into the calcined catalyst. Furthermore, the potential H_2 production was significantly increased by using 5%Ni/dolomite catalyst compared with just the calcined dolomite. In this work the potential hydrogen production is defined as the percentage of the hydrogen produced from the pyrolysis-gasification process in relation to the maximum theoretical amount of H_2 available in the tyre rubber which is estimated to be 38.7 g per 100 g tyre. The introduction of Ni onto the dolomite catalyst was investigated by Wang et al., [16] for cracking of biomass tar using a bench-scale reactor. They reported also that H_2 and CO concentrations were largely increased, whereas methane was reduced with the introduction of 4.1 wt.% of Ni to dolomite.

The reacted calcined catalyst and 5%Ni/dolomite catalyst were characterised by TPO experiments to understand the nature of the carbons deposited on the catalyst surface. Fig. 6

shows the TGA-TPO and DTG-TPO results of reacted calcined dolomite catalyst and 5%Ni/dolomite reacted catalyst. From the TGA-TPO results, the amount of carbon deposited on the catalyst was increased from 3.2 to 6.1 wt.% when the catalyst was changed from calcined dolomite catalyst to 5%Ni/dolomite for the pyrolysis-gasification of waste tyres. The amount of carbon was calculated from the weight loss of sample divided by the initial sample weight in the TGA experiment.

The results of DTG-TPO show that there is a weight loss peak around 710 ^{o}C for the calcined dolomite and 5%Ni/dolomite catalysts (Fig. 6). It is suggested that this weight loss stage was regarded as the dissociation of magnesium carbonate and calcite present in the reacted catalyst [25]. The DTG-TPO results showed also that one oxidation peak was observed for the calcined dolomite and 5%Ni/dolomite catalysts during the pyrolysis-gasification process of waste tyres (Fig. 6). The oxidation peak for the calcined dolomite catalyst occurred at a temperature of about 420 ^{o}C and may be assigned to monoatomic carbon [26]. The oxidation peak for the 5%Ni/dolomite catalyst occurred at about 610 ^{o}C and could be assigned to filamentous carbon [27].

It appears that the oxidation peak which might correspond to the filamentous carbon was not found for calcined dolomite catalyst. This observation is confirmed by the SEM result of calcined dolomite catalyst where no filamentous carbon was found (Fig. 7). It is suggested that the monoatomic carbon is deposited on the surface of the calcined dolomite catalyst and blocks the access of pyrolysis products to the catalyst which explains the lower catalytic activity of calcined dolomite during the pyrolysis gasification of waste tyres.

3.3. Effect of Ni content

As reported in our previous work [28], the gas yield was increased dramatically with an increase in the Ni loading on the Ni/CeO_2/Al_2O_3 catalyst which was used during the pyrolysis-gasification of waste tyres. For example, the gas yield corresponding to the weight of waste tyre was increased from 37.8 to 44.7wt.%, when the Ni loading was increased from 5 to 20 wt.%. It was also found that H_2 concentration increased from 49.46 to 55.97 wt.% and the potential H_2 production increased from 6.13 to 9.46 wt.% as Ni loading was increased.

In this experiment, The influence of Ni loading (5, 10 and 20 wt.%) on the calcined dolomite catalyst was investigated. The mass balances of the experiments with calcined dolomite at different Ni Contents are shown in Table 2. Table 2 indicates that the gas yield in relation to the mass of waste tyre only was increased from 49.1 to 59.4 wt.%, potential hydrogen production was increased from 9.51 wt.% to 12.9 wt.% and the reacted water was increased from 0.21 to 0.29 g, when the Ni content was increased from 5 to 20wt.%. However, the oil yield decreased from 36.7 wt.% to 30.0 wt.% when the catalyst was changed from 5 to 20wt.%.

The concentrations of gases produced from the pyrolysis-gasification of waste tyres at different Ni loading on calcined dolomite catalyst are also shown in Fig. 5. It can be seen that the hydrogen concentration increased from 55.0 to 60.8 vol.%, methane concentration decreased from 13.5 to 8.4 vol.% and hydrocarbon gases (C_2–C_4) decreased from 9.9 to 6.0 vol.%, when the Ni content was increased from 5 to 10 wt.%. However, with the further increase of Ni content to 20 wt.%, hydrogen concentration reduced to 59.0 vol.%, while methane and hydrocarbon gas (C_2–C_4) concentrations slightly increased.

TGA analysis was carried out to characterize the coke deposition on the reacted catalysts. The TGA-TPO and DTG-TPO results are shown in Fig. 6. From the TGA-TPO results, the coke deposited on the catalyst surface was 6.1, 7.9 and 10.1 wt.%, when the Ni loading was 5, 10 and 20 wt.% for the calcined dolomite catalyst respectively. The DTG-TPO results in Fig. 6 show that for the different Ni loaded catalysts, one main oxidation peak was observed at a temperature of about 610 ^{o}C. This oxidation peak might be assigned to the oxidation of filamentous carbon.

The reacted catalysts were also characterized by X-ray diffraction analysis. Fig. 8 shows the X-ray diffraction results from the Ni/dolomite catalysts. The Ni phase was detected in the reacted Ni/dolomite catalyst with different Ni contents (Fig. 8). It is suggested that the NiO phase was reduced to Ni during the gasification process. Similar results were obtained by Wu and Williams [29], where the Ni-Mg-Al-CaO catalyst was investigated in the pyrolysis-gasification of polypropylene. Garcia et al. [30] found that the catalysts used without reduction could be reduced during the steam gasification process by the reaction atmosphere which generates an active surface.

This paper has shown that the amount of coke deposited on a 10%Ni/dolomite catalyst was 7.9 wt.% and the potential H_2 production was 11.38 wt.% at a catalyst:waste tyres ratio of 0.5, gasification temperature of 800 ^{o}C and steam injection rate of 4.74 g h^{-1}. Comparison may be made with the dolomite support used in this work with alumina. Our previous work [28] showed that under the same operational conditions and also with waste tyres as the feed stock that 18.2 wt.% coke and 7.18 wt.% potential H_2 production was obtained using a 10%Ni/Al_2O_3 catalyst. In addition, with incorporation of cerium into the nickel alumina catalyst the coke formation on the catalyst was reduced to 14.0 wt.% and the potential hydrogen production was increased to 8.20 wt.% using a 10%Ni/15 %CeO_2/Al_2O_3 catalyst. Consequently, for the pyrolysis-gasification of waste tyres, nickel dolomite catalysts produce less coke on the catalyst and a higher production of hydrogen compared to nickel alumina catalysts. Srinakruang et al. [18] also reported superior catalytic activity for a nickel dolomite catalyst compared to a nickel alumina catalyst. They reported that the Ni/dolomite catalyst showed excellent catalytic activity, durability and resistance to coke formation and sulfur poisoning in comparison with Ni/Al_2O_3 and Ni/SiO_2 catalysts. Therefore, compared with the other supported catalysts, Ni/ dolomite showed higher activity and coking resistance. However, it should be noted that from Fig. 9, sulfur was detected on the surface of used Ni/dolomite catalyst by the EDXS analysis. Therefore, the deactivation of the catalysts used during the gasification of waste tyres might not be mainly due to the deposition of coke on the catalyst but due also to sulfur poisoning. This effect of sulfur poisoning of the catalysts is to be addressed in a future publication.

4 Conclusions

In this paper, hydrogen production from the pyrolysis-gasification of waste tyres has been investigated with a nickel/dolomite catalyst using a two-stage fixed bed reaction system. The calcined dolomite and Ni content in the calcined dolomite catalyst were characterized and investigated for their influences on gas, hydrogen production and coke deposition on the surface of the catalyst. It was concluded that:

1- XRD of fresh dolomite, calcined dolomite and 10%Ni/dolomite catalysts showed the presence of only CaO and MgO phases in calcined dolomite confirming the decomposition of dolomite which was also confirmed by TGA-TPO analysis. XRD showed also the presence of spinel phase ($NiMgO_2$), NiO, CaO and MgO in the 10%Ni/dolomite catalyst.

2- The gas yield was significantly increased from 30.3 to 49.1 wt.% and the potential H_2 production was significantly increased by introduction of 5%Ni into the calcined dolomite catalyst. Furthermore, much higher Ni contents up to 20 wt.% increased the catalytic activity, and lead to higher hydrogen production from pyrolysis-gasification of waste tyres.

3- The amount of coke deposited on the catalyst surface was 3.2, 6.1, 7.9 and 10.1 wt.%, when the Ni loading was 0, 5, 10 and 20 wt.% on the calcined dolomite catalyst respectively.

The calcined dolomite catalyst was deactivated by monoatomic graphitic carbons, whereas calcined dolomite with different Ni loadings were deactivated by filamentous carbons.

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Table 1

BET surface area of research catalysts.

Catalyst	Loading of Ni (wt.%)	BET surface area (m^2g^{-1})
Calcined dolomite	0	6.0
5%Ni/dolomite	5	32.6
10%Ni/dolomite	10	38.2
20%Ni/dolomite	20	31.8

Table 2

Mass balances at different Ni content for the two-stage pyrolysis-gasification of waste tyre.

Ni content (wt.%)	0	5	10	20
Mass balance in relation to tyre + water				
Gas/(tyre + water) (wt.%)	27.0	40.7	40.0	46.0
Solid/(tyre + water) (wt.%)	33.6	27.7	30.4	26.9
Oil/(tyre + water) (wt.%)	34.0	30.4	26.2	23.2
Mass balance (wt.%)	94.7	98.8	96.6	96.2
Mass balance in relation to tyre only				
Gas/tyre (wt.%)	30.3	49.1	50.1	59.4
Solid/tyre (wt.%)	37.7	33.5	38.0	34.7
Oil/tyre (wt.%)	38.2	36.7	32.7	30.0
Mass balance (wt.%)	106.2	119.3	120.8	124.0
Reacted water (g)	0.12	0.21	0.26	0.29

Figure Captions

Fig. 1. Schematic diagram of the two-stage pyrolysis-gasification experimental system

Fig. 2. SEM-EDXS results of the fresh catalysts at different Ni contents

Fig. 3. TGA-TPO and DTG-TPO results of the fresh dolomite

Fig. 4. XRD results of the fresh catalysts; (a) Dolomite; (b) Calcined dolomite (c) 10%Ni/dolomite

Fig. 5. Gas concentrations at different Ni contents

Fig. 6. TGA-TPO and DTG-TPO results of the reacted catalysts produced at different Ni contents

Fig. 7. SEM results of the reacted catalysts at different Ni contents

Fig. 8. XRD results of the reacted catalysts; (a) Calcined dolomite; (b) 5%Ni/dolomite; (c) 10%Ni/dolomite; (d) 20%Ni/dolomite

Fig. 9. EDXS results of the reacted catalysts at different Ni contents

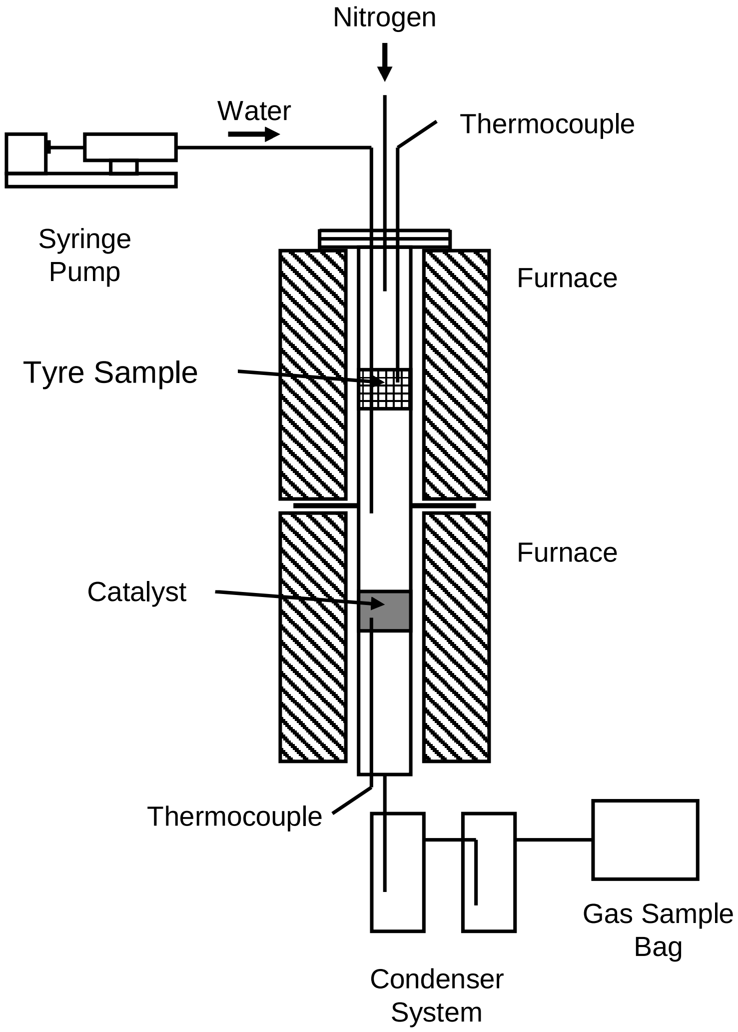

Fig. 1 Schematic diagram of the two-stage pyrolysis-gasification experimental system

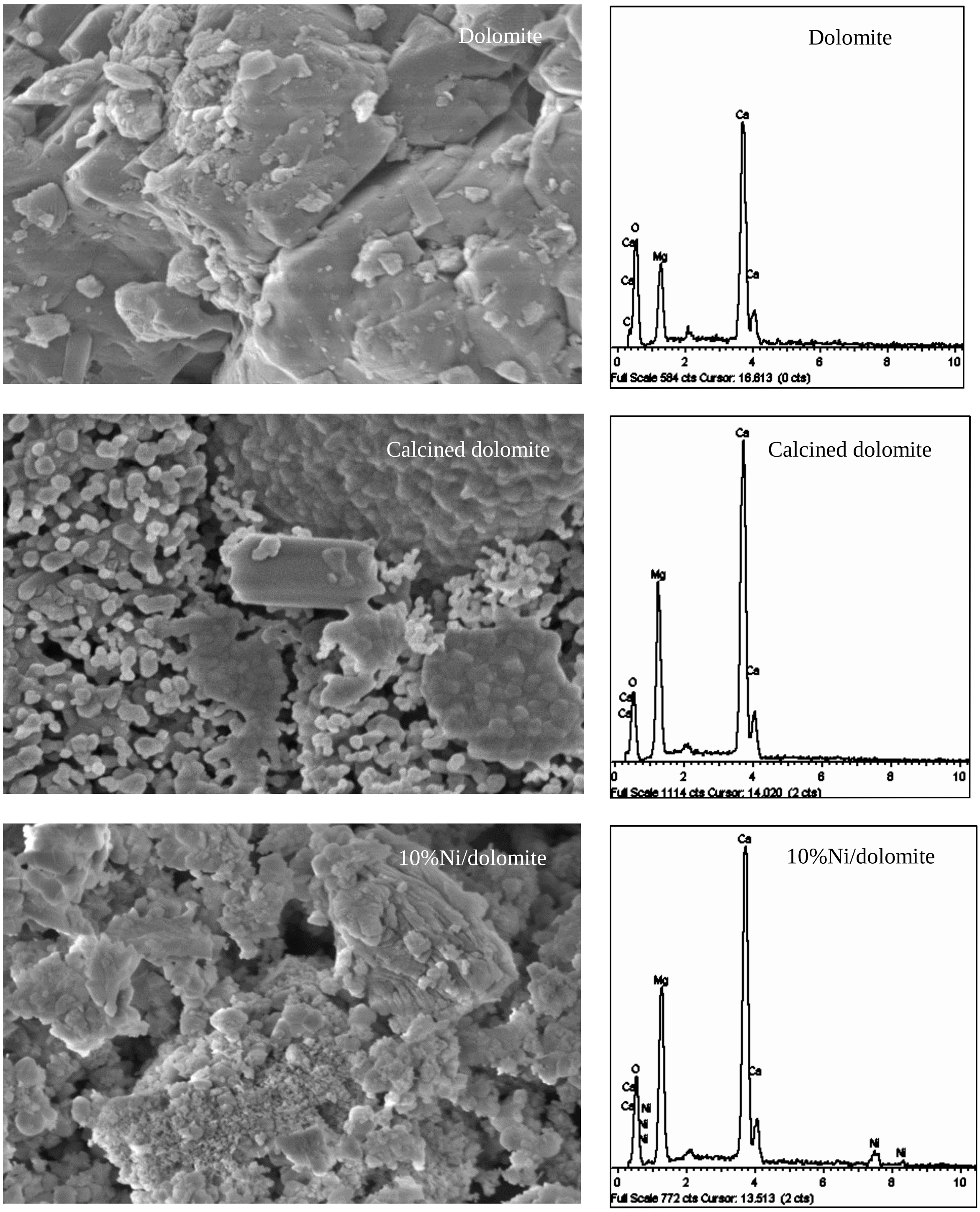

Fig. 2 SEM-EDXS results of the fresh catalysts at different Ni contents

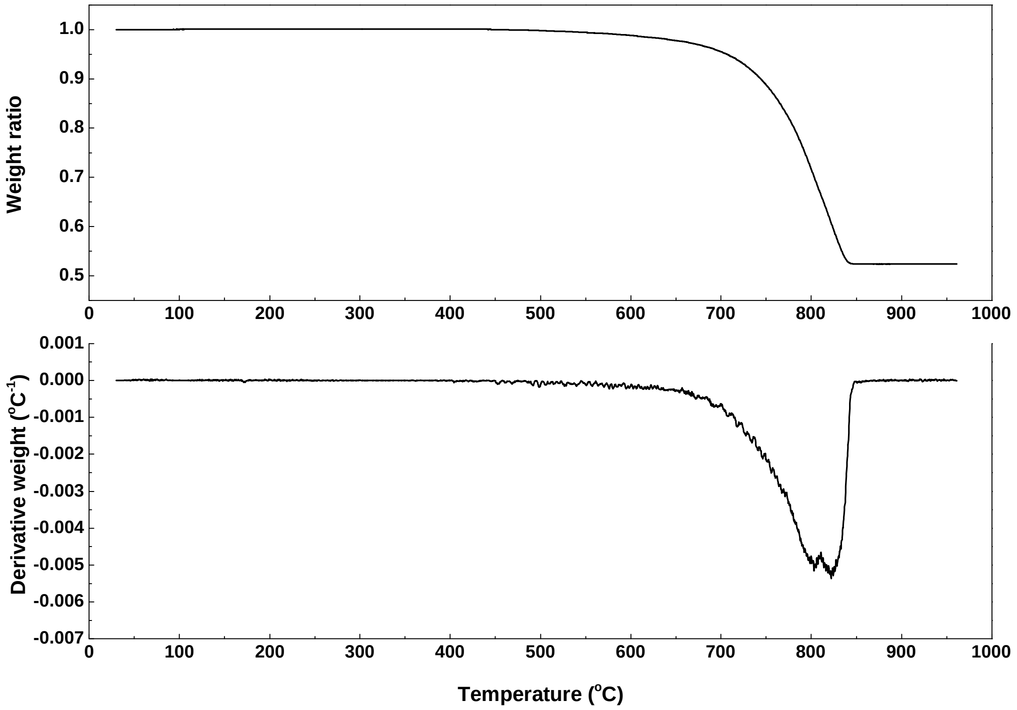

Fig. 3 TGA-TPO and DTG-TPO results of the fresh dolomite

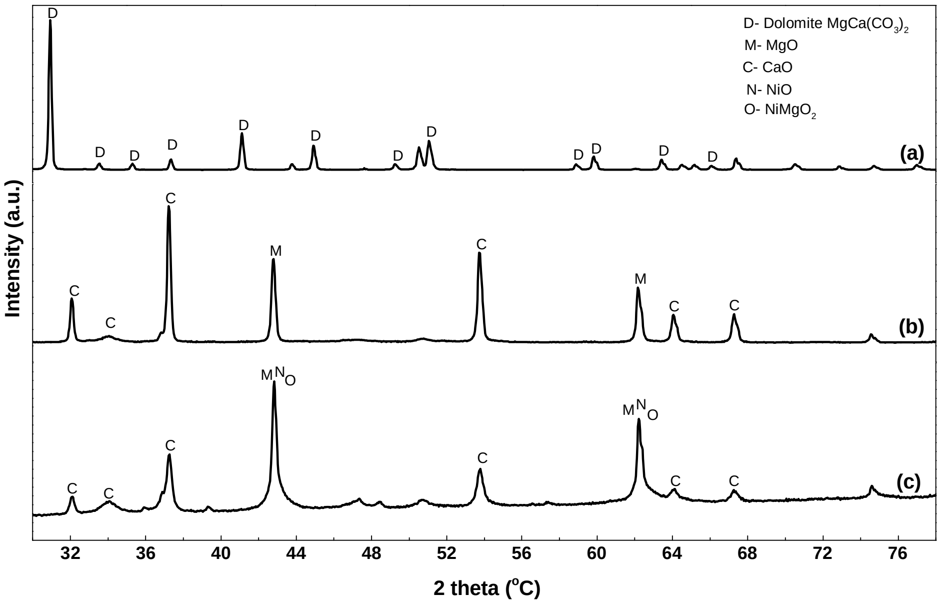

Fig. 4 XRD results of the fresh catalysts; (a) Dolomite; (b) Calcined dolomite (c) 10%Ni/dolomite

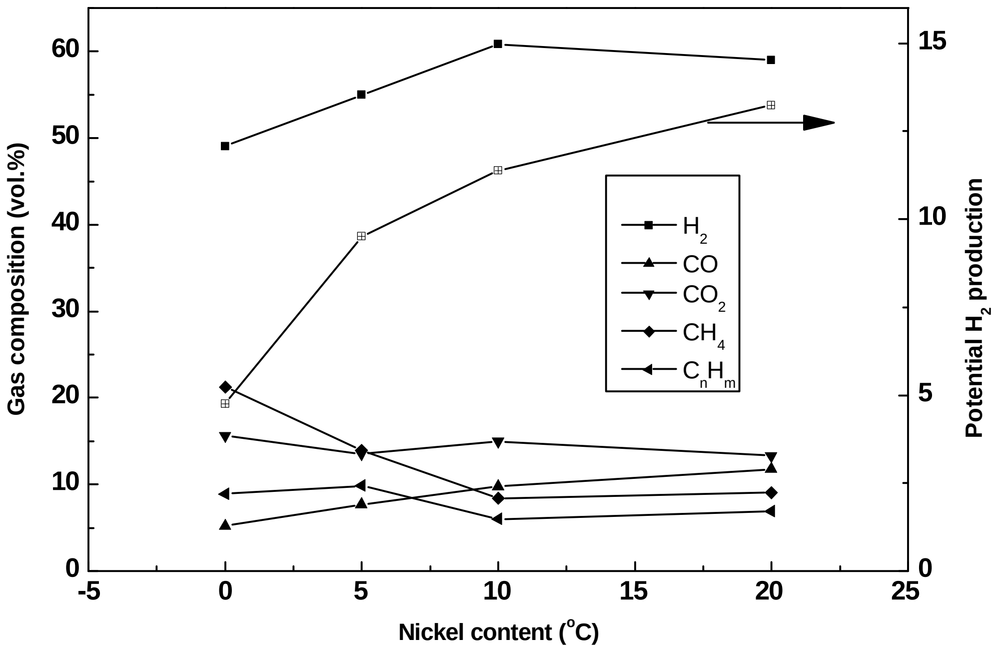

Fig. 5 Gas concentrations at different Ni contents

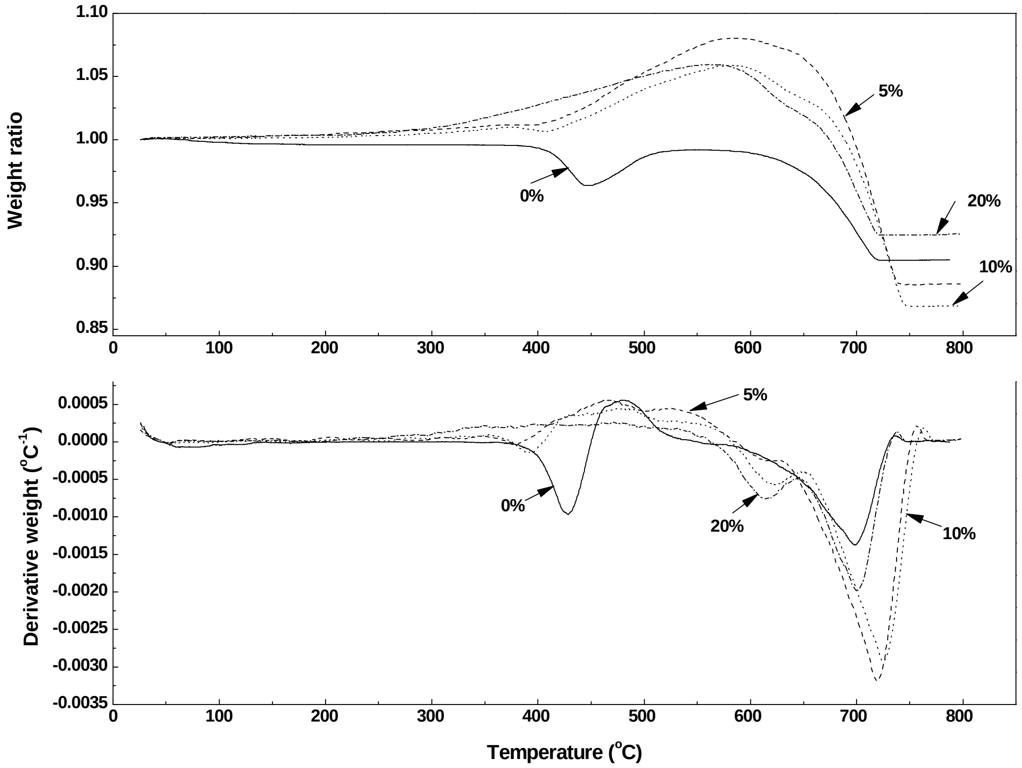

Fig. 6 TGA-TPO and DTG-TPO results of the reacted catalysts produced at different Ni contents

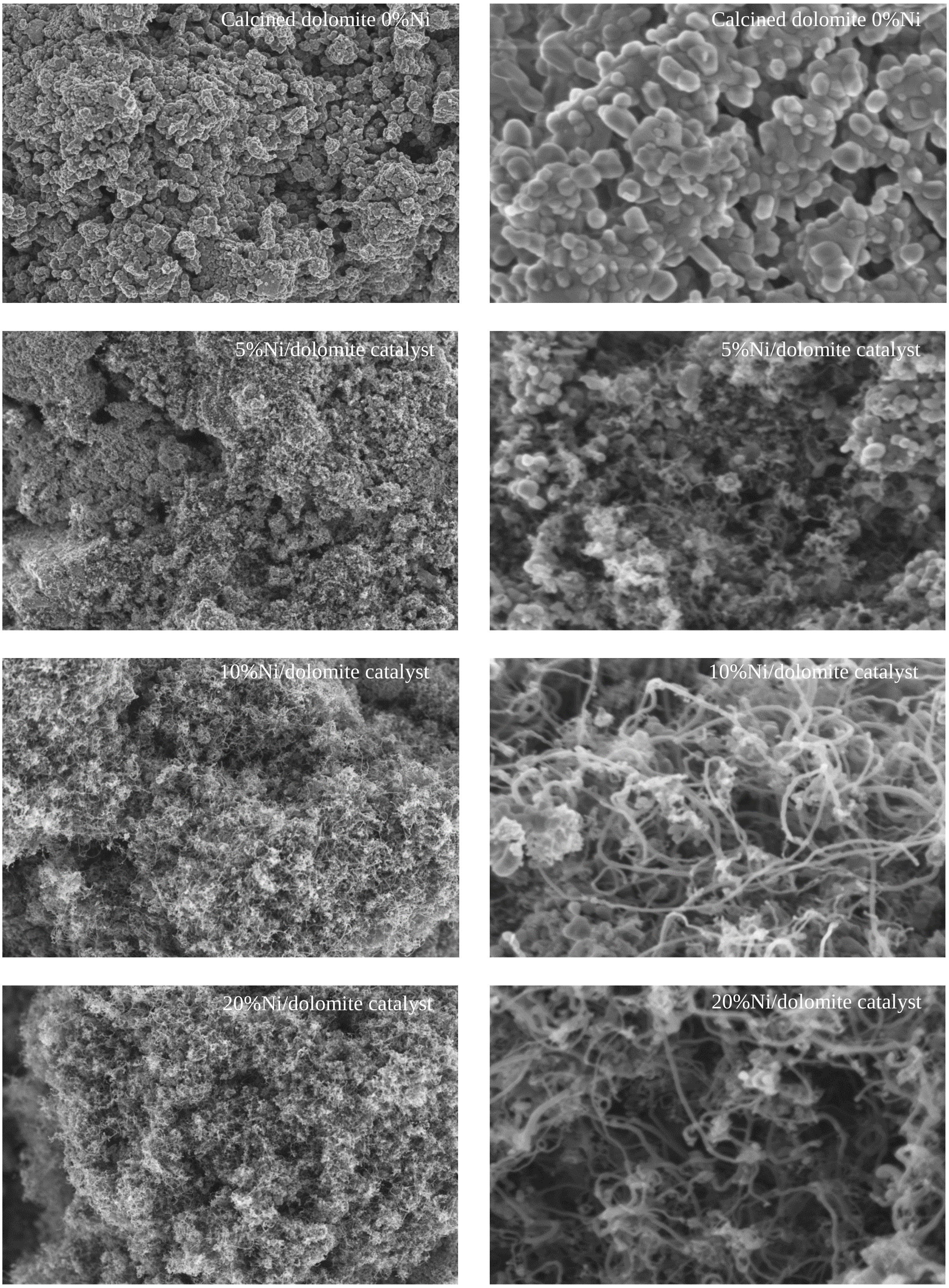

Fig. 7 SEM results of the reacted catalysts at different Ni contents

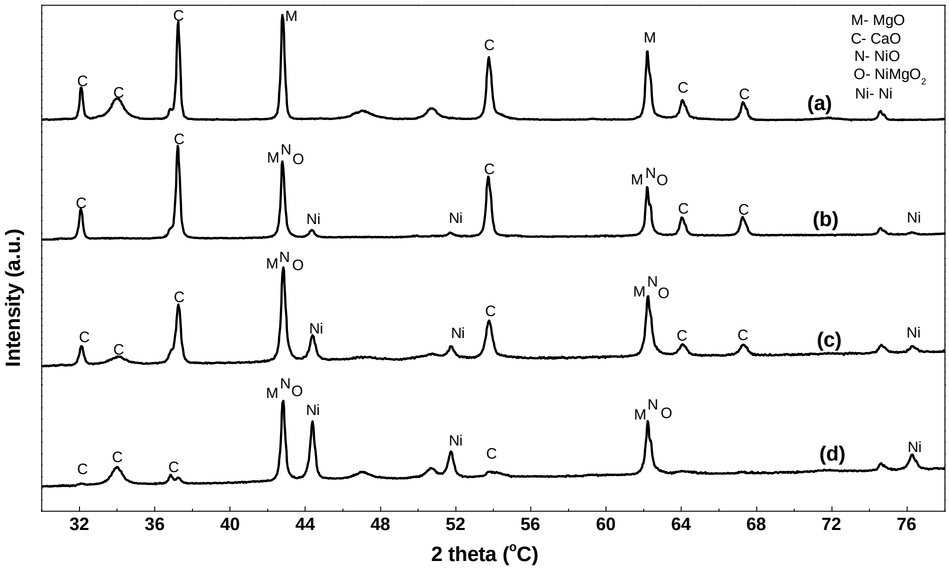

Fig. 8 XRD results of the reacted catalysts; (a) Calcined dolomite; (b) 5%Ni/dolomite; (c) 10%Ni/dolomite; (d) 20%Ni/dolomite

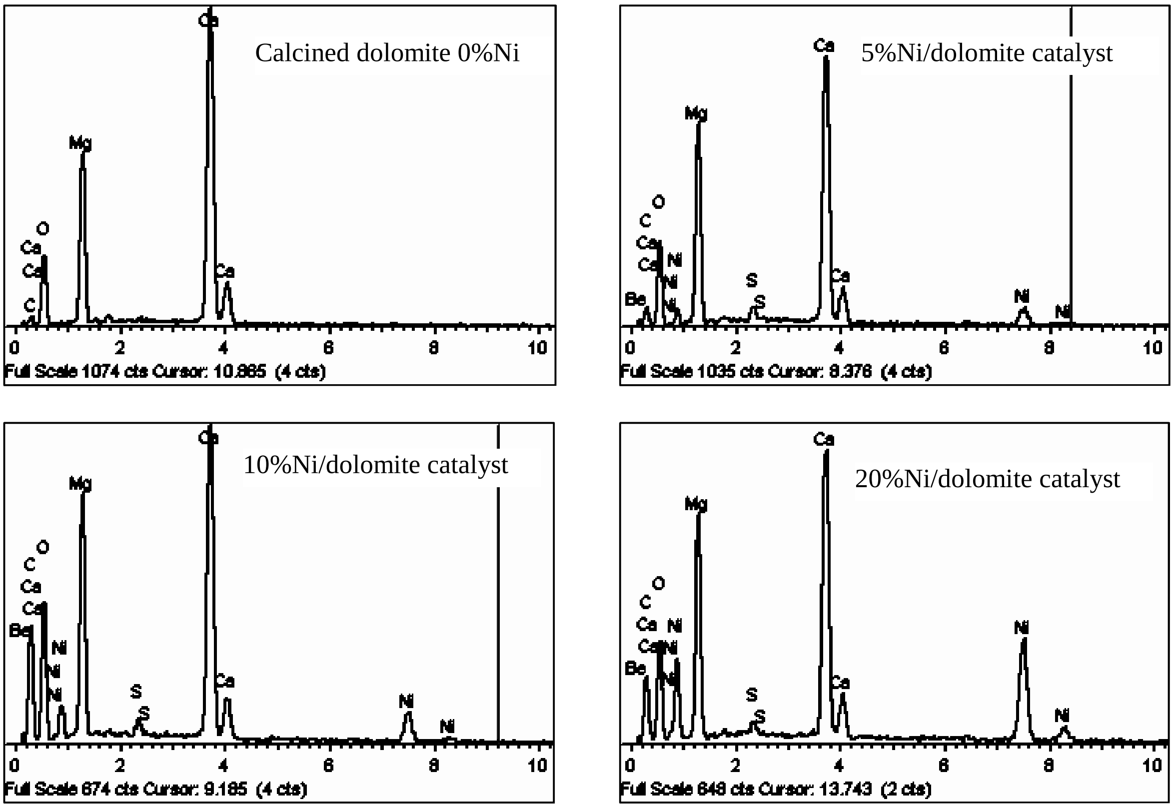

Fig. 9 EDXS results of the reacted catalysts at different Ni contents.