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Synergic effect of heat and light on the catalytic reforming of methanol over Cu/x-TiO₂(x = La, Zn, Sm, Ce) nanocatalysts



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the CO_2 selectivity by about 99.9 %.

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ARTICLE INFO	A B S T R A C T
Keywords:	Hybrid photo-thermal-catalytic reforming of methanol was investigated by Cu/TiO ₂ nanocatalysts. The obtained
Photo-thermal catalysis	results indicated that methanol conversion (150 °C) was remarkably increased by congruent roles of the photo
TiO ₂ support	and thermal catalysis (about 36 % in the presence of light). To gain further insight into this effect, the semi-
Methanol reforming	conductor properties of TiO ₂ nanoparticles were modified with dopants (Ce, La, Sm and Zn). Cyclic voltammetry
Cu catalyst	was also adopted as a mean of studying the semiconductor properties of these doped TiO ₂ nanoparticles. The
Hydrogen production	reactor tests of these Cu/doped-TiO ₂ nanocatalysts confirm that their activity and selectivity are highly de-
Hydrogen production	pendent on the semiconductor properties and surface defects of TiO_2 nanoparticles. Accordingly, the CO_2 se-
	lectivity depends on the surface defects of TiO ₂ and Al ₂ O ₃ /TiO ₂ support with the high surface defects improves

1. Introduction

Excessive consumption of fossil fuels uses up non-renewable sources of energy on one hand and pollutes the environment on the other. Therefore, there is a great interest in the production of energy via other methods. These have caused the emergence of hydrogen as an alternative source of energy. There are several commercialized hydrogen production methods from methane and other hydrocarbon sources such as gasoline, and diesel. Another reported method for hydrogen production is methanol reforming [1-3]. Compared with other hydrogen sources, methanol has numerous advantages, the most important of which is the lack of a strong C-C bond. Thus, methanol conversion can be carried out at relatively low temperatures (under 400 °C). This temperature range is lower compared with that required for the conversion of methane to hydrogen by steam reforming, which usually takes place at temperatures of around 800 °C. Also, methanol properties such as: being liquid and having high hydrogen to carbon ratio has made it a serious choice for hydrogen production [4-7].

Steam reforming of methanol (SRM) and photo-catalytic reforming of methanol are two advanced procedures of methanol reforming [8–10]. The SRM reaction is performed with a heterogeneous catalysis involving solid phase catalysts and gas phase reactants. Copper catalysts are the most conventional catalysts for SRM reaction, which are deposited on a porous support such as Al₂O₃ [11,12]. The photocatalytic reforming of methanol is commonly achieved with a solidliquid heterogeneous catalysis process, which photo-active metal oxides (support) such as TiO₂ in conjunction with noble metals play the photocatalyst role [13]. The advantage of photo-catalytic reforming of methanol process is that it can be performed at low temperature (room temperature) conditions. The operating temperature for the SRM process is higher than photo-catalytic reforming, but the SRM process has other advantages such as higher methanol conversion rate, appropriate selectivity and inexpensive catalyst (copper). Considering that these methods have different advantages, a hybrid photo-thermal-catalytic reforming of methanol can have a combination of those advantages. Among the steam reforming catalyst supports, TiO₂ is a photo-active support and displayed the highest activity in the photo-catalytic reforming of methanol. Furthermore, TiO₂ is regarded as an excellent supporting material for the reduction of coke formation [10]. Recently, porous TiO₂was used as catalyst support in SRM reaction, which presented high conversion and selectivity [14,15]. Scott et al. found that the photoexcitation of Au/TiO2 catalyst improves the thermal-catalytic oxidation of ethanol [16]. Greaves et al. showed an increase in methanol conversion when an Au/TiO2 photo-catalyst was illuminated in contact with methanol-water vapors (25 °C), with respect to liquid suspension [17]. The effects of noble metals in the photocatalytic steam reforming of methanol were investigated by Selli et al., revealing that metal activity depends on their work function and Pt is the most

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effective co-catalyst compared to gold and silver [18].

The work function of copper (4.7 eV) placed between Ag (4.3) and Au (5.1), which indicated that Cu in conjunction with TiO_2 is an appropriate choice for the hybrid photo-thermal-catalytic reforming of methanol. Also, a porous synthesized TiO_2 film, which deposited on a monolith reactor, can improve the catalyst activity with its high surface area [14]. The most important subject in hybrid photo-thermal-catalytic reforming reactors is the ability of reactor to pass light. As a matter of fact, since monolithic reactors are formed by a series of connected channels, they have advantages such as passing light, low pressure drop, heat and mass transfer, and suitable contact between the reactants and catalyst surface [19,20].

Furthermore, the properties of synthesized TiO_2 could be changed and improved with doping elements into the TiO_2 structure [21]. The nature of TiO_2 nanoparticles and dopants mainly affects the electronic structure and trap states of TiO_2 film. Specially, the lower edge of the conduction band and density of states (DOS) of TiO_2 are made up of titanium 3d orbitals. Thus, replacing titanium cation with other cations (with various 3d orbitals) is expected to significantly affect these states of TiO_2 [22]. Furthermore, dopants increase the surface defects on TiO_2 surface. These defects have different interactions with reagents such as water, oxygen and carbon monoxide [23].

The addition of ZnO improves the Cu dispersion and increases the so-called "spill over" effect by enhancing the reducibility of the CuO precursor [24–26]. In general, methanol adsorption presumably takes place on the copper metal, followed by dissociation of hydrogen atoms from the adsorbed methanol and their movement (spill over) from the copper onto the ZnO, in which they are lightly bound [27]. The ability of the Ce element to undergo facile conversion between Ce⁺⁴ and Ce⁺³ oxidation states, makes it another appropriate choice as promoter in the SRM reaction. For instance, Ce₂O₃ dimers over TiO₂ surface displayed high activity toward the water-gas shift (WGS) reaction because H₂O can easily dissociate on Ce³⁺ sites [28]. Lanthanum is another interesting promoter because of its strong binding strength to oxygen. Also, when La³⁺ is doped into the TiO₂ structure, it will scavenge surface oxygen and induce vacancies [29].

Understanding the major features and properties of TiO₂ and doped-TiO₂ nano-porous films could be achieved by investigating the fundamental electrochemical techniques such as cyclic voltammetry (CV). The CV technique provides sufficient data for a qualitative and quantitative characterization of these films. The voltammograms of TiO₂ films could provide information about the densities of localized states in the conduction band, densities of surface states/traps and resistance (including series resistance in CV condition) of TiO₂ [30]. These properties of TiO₂ play an important role in TiO₂ activity in chemical and photo chemical reactions [31]. Localized states in the conduction band accept electrons from other material and transfer them through the TiO₂ conduction band. Surface states/traps are TiO₂ surface defects, which are produced with oxygen vacancy [32]. These traps exhibited different interactions with reagents (such as CO, H₂O, NO) and catalyzed some reactions, which could not be performed on surfaces without defects. [24]

In this work, considering the importance of methanol reforming in hydrogen production, a hybrid photo-thermal-catalytic process for methanol reforming was designed. Hence, some Cu/porous TiO₂/ monolith structures were prepared as hybrid photo-thermal catalyst and characterized. The activity and selectivity of these catalysts were investigated and compared in light and dark conditions. In addition, the catalytic performances of Cu/TiO₂-synthetic/monolith and Cu/TiO₂-Sigma/monolith have been compared from the activity and selectivity perspectives under identical conditions. To further investigate the effect of TiO₂ on selectivity and activity in methanol reforming, doped TiO₂ nanoparticles with La, Sm, Ce and Zn elements have been synthesized and evaluated in a Cu/doped-TiO₂/monolith catalyst system. Meanwhile the density of states, resistance and surface defects of these TiO₂ films have been determined using cyclic voltammetry. From the observed activity and selectivity of these TiO_2 nanoparticles we deduce further details of the role of TiO_2 in methanol reforming. Meanwhile the structural characteristics of the synthetic catalysts have been determined using cyclic voltammetry, TGA, FE-SEM, BET, XRD AFM, TEM, EDSX and TPR analyses as well as reactor tests.

2. Experimental

2.1. Materials

All materials were purchased from Merck and Sigma-Aldrich chemical companies and were used as received. The materials used included Samarium(III) nitrate hexahydrate [Sm(NO₃)₃·6H₂O, 99.997 % trace metals basis], Zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O], lanthanum nitrate hexahydrate [La(NO₃)₃.6H₂O, 98 %], Cerium(III) nitrate hexahydrate [Ce(NO₃)₃·6H₂O], Cu(NO₃)₂.6H₂O, titanium isopropoxide(TIP) and α -terpinol, TiO₂ Sigma-Aldrich.

2.2. Synthesis of X-TiO₂(x = La, Zn, Sm, Ce)

TiO₂ and doped TiO₂ nanoparticles were synthesized by a modified method [14]. 6.1 g of glacial acetic acid were mixed with 30 g of titanium isopropoxide (TIP). The obtained precursor was poured into a solution of 150 ml of DI water, 3 ml of nitric acid (65 %) and 0.42 g of dopant metal salts. After mixing for 45 min, the temperature was slowly increased to 60 °C and the solution was refluxed for 2 h. The mixture was then transferred to a 300 ml autoclave and the resulting mixture was heated at 180 °C for 10 h. The colloidal solution was then sonicated and centrifuged again to remove large undesirable particles. After drying at 80 °C, the TiO₂ slurry was prepared using a previously reported method [33,34].

2.3. Synthesis of Al₂O₃/TiO₂

Porous alumina (BET surface area about 350 m²/g) was synthesized by a reported method [33]. 1 g of this alumina was treated with a TiCl₄ solution (5 × 10⁻⁶ M in 70 °C). After 10 min, the treated alumina was separated and washed with DI water. The resulted white precipitate was dried in 80 °C and calcined at 500 °C for 30 min.

2.4. Monolith washcoating by X-TiO₂(x = La, Zn, Sm, Ce) supports

Cordierite monolith samples (Corning USA, 400 cps) were cut in $3 \times 0.7 \times 0.7$ cm dimensions. Dry monolith was slowly deep coated into the X-TiO₂ (X = La, Zn, Sm, Ce) slurries for 1 min and the excess of slurry was then slowly removed from the monolith channels by air blowing and dried at 120 °C for 12 h. The samples were calcined at 500 °C for 2 h to establish a layer of the supports with suitable adhesion on the monolith channel walls. To synthesize Cu/X-TiO₂(x = La, Zn, Sm, Ce) catalysts, the prepared monoliths were impregnated in 1 M Cu (NO₃)₂.6H₂O solution by the wet impregnation method. After removing the monoliths from the solution, they were dried in a microwave oven at 200 W for 10 min and calcined in air at 300 °C for 2 h (Microwave drying results in fast and uniform drying which results uniform distribution of metal).

2.5. Activity measurements

Details of reactor setup and reaction conditions have been described in the supporting information (Fig. S1). Also, all the tests, in the presence or absence of light, have been carried out in a monolith reactor. In photo-catalytic conditions, an LED jacket (with different lamp covering 380 - 700 nm) was placed on top of the reactor. The whole reactor and LED jacket were covered with aluminum foil. The intensity of light on top of the monolith reactor was 80 lx.

2.6. Characterization

To identify phases and crystallinities of the samples, X-ray diffraction analyses were performed by an INEL EQUINOX 3000 X-ray diffractometer using Cu K α radiation ($\lambda = 1.5406$ Å) in the 2 θ range of 5-80°. The surface area, pore volume and pore diameters were estimated by the BET (Brunauer-Emmett-Teller) method from nitrogen adsorption-desorption isotherms data obtained at -196 °C on a constant-volume adsorption apparatus (Micromeritics Instrument Corporation TriStar 3020). Prior to the adsorption-desorption measurements, all the samples were degassed at 200 °C under N2 flow for 3 h. Field emission scanning electron microscopy (FE-SEM) micrographs were obtained using Philips (XL30) and Zeiss instruments, under vacuum, accelerated at 20 and 15 kV, respectively. The transmission electron microscopy (TEM) images were taken by a Zeiss, EM 900 transmission electron microscope (TEM) apparatus. Atomic force microscope (AFM) was performed in a DPN 5000, working in the non-contact mode with standard silicon tips. All samples were washed and cleaned by DI water before AFM images were taken.

The amounts of carbon deposited on the surfaces of the used catalysts were evaluated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in an air atmosphere at a heating rate of 10 °C/min up to 800 °C on a TG-DTA SDTA 851e instrument. The bulk reduction behavior of each catalyst was studied using a BELCAT-A system. 0.05 g of each calcined sample was initially heated under a helium flow (40 N mL/min) at a rate of 10 °C/min to 200 °C for 20 min. The reducing gas (5 % H₂ in Ar) was then switched at 50 N ml/min and the temperature was raised at a rate of 10 °C/min up to 800 °C. The effluent gas was passed through a cooling trap (at a temperature lower than -50 °C) to condense and collect the water generated during the reduction process. A thermal conductivity detector (TCD) was used to determine the amount of H₂ consumed.

Cyclic voltammetry spectra were acquired with a μ Autolab Type III in a three-electrode electrochemical cell in the dark. The working electrodes were prepared by screen printing of TiO₂ paste on fluorinedoped tin oxide (FTO) coated glass (area of the TiO₂ films: $4 \times 8 \times 0.0025$ mm). The photoanodes were then calcined at 500 °C for 15 min. Saturated Ag/AgCl and Pt electrodes were employed as the reference and counter electrodes, respectively. The electrolyte solution consisted of 1 M KCl at pH: 2.

3. Results and discussion

3.1. Characterization

The X-ray powder diffraction (XRD) images of the CuO/TiO₂ and CuO/TiO₂-doped catalysts are shown in Fig. 1. The XRD patterns clearly reveal that all TiO₂ nano-crystals exist in anatase phase (JCPDS# 21-1272). The anatase phase has been preserved during the calcination



Fig. 1. XRD patterns of synthetic Cu/Sigma-TiO $_2$ and Cu/X-TiO $_2$ (X = La, Zn, Sm, Ce) catalysts.

process in all samples, indicating the stability of these supports. At 0.5 wt. % of the dopant, there are no noticeable peaks for the metal oxides of dopants, which indicates that the metal oxides of dopants are distributed in host, amorphous or both. The average crystal size of TiO₂, doped-TiO₂ and CuO deposited TiO₂ catalysts were calculated using Debye-Scherer equation and the results are summarized in Table 1. The crystal size of the doped-TiO₂ (about 12 nm) was reduced compared with that of the pure TiO₂ nanoparticles (about 14 nm). Dopants often decrease the growth rate of the TiO₂ crystals, resulting in smaller crystals sizes [35]. An exception is observed in the Zn-doped sample, which has a crystal size of about 14 nm. Owing to the similar size of Zn^{2+} and Ti⁴⁺ ions, the lattice distortion defects in doped-TiO₂ with Zn are negligible compared with other dopants. Therefore, the impact of these defects in the crystal growth decreases, resulting in a similar crystal size for pure and Zn-doped TiO₂. The calculated average crystal sizes of CuO particles on TiO₂ supports are displayed in Table 1; accordingly, the crystal sizes are 24-29 and 21 nm for the synthesized supports and commercial Sigma sample, respectively.

The morphology and surface structure of the catalysts were investigated using AFM and FESEM analyses. The commercial TiO_2 sample (CuO/Sigma-TiO₂) has a different morphology compared with the synthesized samples because of the large particles size of the commercial sample (see Fig. 2). The AFM and FESEM images of the synthesized samples are displayed in the supporting information (Figs. S2). All synthesized TiO_2 samples presented the same surface morphology with almost similar particles sizes.

The addition of the dopants to the TiO_2 structure was investigated by energy-dispersive X-ray spectroscopy (EDS) and the spectra are displayed in Fig. 3, and Fig. S3. The spectra reveal that the Ti, O and Cu atoms exist in all the samples. Quantitative analyses of these EDS spectra indicate that the weight percentages of the dopant in CuO/Ce-TiO₂, CuO/La-TiO₂, CuO/Sm-TiO₂ and CuO/Zn-TiO₂ are 0.5, 0.6, 0.5 and 0.9 %, respectively (see Table 1).

Fig.S4, shows the N₂ adsorption-desorption isotherms of synthetic TiO_2 and Cu/X- TiO_2 (X = La, Zn, Sm, Ce) nanocatalysts used for the determination of the BET surface areas, average pore sizes and pore volumes, as summarized in Table 1. As observed, the synthetic TiO_2 support has a much larger surface area, pore size and pore volume compared with Sigma sample, which improves the distribution and dispersion of the active metals on the support surfaces [36]. It is apparent from Table 1 that the specific surface area as well as pore volume of the support decreases after 10 % Cu impregnation. As anticipated, the wet impregnating of Cu active metal has resulted in dropping the surface area/pore volume by blocking the support surface/pores by means of the metal oxide nanoparticles [37].

The TiO₂ samples are deposited on the FTO surface as working electrodes for cyclic voltammetry (CV) studies. All measurements were performed under the same conditions (dark environment, saturated KCl solution and pH = 2) and the obtained cyclic voltammograms are depicted in Fig. 4. Furthermore, the obtained data are summarized in Table 2. All the voltammograms show a peak in the range of 0.7–1.2 V, which can be attributed to the surface state traps of TiO₂ particles [33,38,39]. The oxygen vacancies are the reason for these traps (defects), which produce Ti⁺³ at the fivefold and sixfold surface Ti in the vicinity of the vacancies [40,41]. Integration of the surface state trap peaks indicates that the area and development of these peaks are different in the investigated samples. The Ce-TiO₂ sample presented the highest development of these traps (4.5×10^{-4}) while La-doped sample (3.9×10^{-4}) displayed the lowest trap development. These traps can act as catalyst sites and interact with some molecules such as NO and CO [23].

The cathodic current of TiO_2 film depends on the density of the localized states (DOS) of TiO_2 film [42].The current of the purely capacitive TiO_2 electrode is solely formulated from the capacitance response of the CV (Eq. 1):

Table 1

Specific surface areas of supports and supported catalysts.

Sample	Active metals (%)	Dopant ^a (%)	BET Surface area(m ² /g)	Total pore volume (cm ³ /g)	Pore size (nm)	TiO ₂ Size from XRD (nm)	CuO Size from XRD (nm)
TiO ₂ (Sigma)	10.2	0	9.9	0.04	16.9	85	21
TiO ₂ (Synthetic)	10.4	0	83.9	0.5	24.1	14.2	27
Cu/Zn-TiO ₂	10.7	0.6	46.8	0.45	23.6	14	28
Cu/Sm-TiO ₂	10.5	0.5	50.4	0.3	21.4	12.2	29
Cu/La-TiO ₂	10.5	0.6	51.4	0.26	20.2	12.8	25.9
Cu/Ce-TiO ₂	10.6	0.5	62.9	0.41	22.5	12.2	23.7

^a calculated from EDS results.

$I = \frac{dQ}{dt} = Cs$	(1)
	· · · · · · · · · · · · · · · · · · ·

Where *s* is scan rate in CV and *C* is the capacitance of the TiO_2 electrode. The capacitance behavior of the TiO_2 electrode is directly related to DOS in the conduction band. Consequently, the corrected cyclic voltammograms between -1.5 - 0 V (with respect to the standard Ag/

AgCl electrode) display the DOS of the prepared electrode [30].The integration of these calculated DOSs are presented in Table 2. The DOS of the TiO₂ conduction band (CB) is composed of empty orbitals of titanium and oxygen. The lowest states of the CB involve Ti t₂g states, having metal-metal interaction [43]. The lowest states of the CB play important roles in electron accepting [33] and electron transfer [44]



Fig. 2. FESEM (top), 2D AFM (middle) and 3D AFM (bottom) images of the synthesized Sm-TiO₂ sample (left) and commercial TiO₂ sample (right).



Fig. 3. EDS and FESEM image of Cu/La-TiO₂ and Zn/TiO₂ samples.



Fig. 4. Cyclic voltammograms of Cu/Ce-TiO₂, Cu/La-TiO₂, Cu /Sm-TiO₂ and Cu /Zn-TiO₂ nanocatalysts.

Table 2

Integral of cyclic voltammograms peaks and calculated resistance of doped samples.

Sample	Localized states	Surface states	Resistance (Ω)
Synthetic TiO ₂	2.09	0.39	104
Zn-TiO ₂	1.63	0.46	176
Sm-TiO ₂	2.03	0.43	136
La-TIO ₂	2.13	0.38	82
Ce-TiO ₂	1.71	0.45	153

properties of TiO_2 . Accordingly, doped metals in the TiO_2 structure could considerably influence these states.

The resistance of TiO₂ film in CV condition can be calculated from cyclic voltammograms by a previously reported method [44]. This calculated resistance is the sum of several resistance connecting in series arrangement (such as TiO₂ resistance and electrolyte resistance). Because the CV studies were performed in the same solution, the difference in calculated resistance is related to the TiO₂ resistance. The TiO₂ resistance depends on the concentration of the electrons in the CB (generated by both bulk and surface defects), porosity, particles grain boundary and particle size. The obtained resistance of the doped sample is presented in Table 2, indicating that the resistance of the samples was changed by dopants. This is because the electrons are transferred through the titanium t_{2g} orbitals in the conduction band. So, changing the t_{2g} metal-metal interaction with metal dopants can influence the electron transfer pathways. Also, dopants modified the porosity, surface area and crystal size of the TiO2 particles influencing the TiO2 resistance. The TiO₂ and La-TiO₂ samples have the lowest resistance. The low resistance of the La-TiO2 sample is related to low porosity (according to BET results), high surface defects (please see CV data) and appropriate crystal size (according to XRD patterns) reducing the TiO₂ layer resistance. Among doped TiO₂ samples, the Zn and Ce samples gave the highest resistance. These results are consistent with other reports in which Ce and Zn as dopants, enhance the electrical resistance of TiO_2 [45,46]. Ce as the dopant can increase the resistivity of TiO_2 by a factor of about 300. This is due to the new oxygen vacancies and electron traps, which are simultaneously introduced with Ce doping. These two effects increase the TiO₂ resistance with Ce doping [47].

Fig. S5, Shows the TEM images of TiO_2 support, $CuO/Sm-TiO_2$ and CuO/TiO_2 . As observed in the images, the addition of Sm promoter to the structure of TiO_2 support maintains the nanometric sizes of the support. In addition, uniform and homogeneous distribution of the



(C)

Fig. 5. SEM microscope images of: (A) blank monolith, (B) and (C) monolith with TiO₂ support.

active metal on the support observed for Sm-dopant sample. Also as shown in Fig. **S**5, achieving a structure with a particle size below 25-35 nm of TiO₂ support has allowed vast dispersions of the active metal on the support. By comparing the TEM images of Fig. **S**5 catalysts, it is possible to observe the proper dispersion of the Cu active metal on the catalysts. This results in the uniform distribution of the metal active phase on the support, and leads to better catalytic performance.

Fig. 5A, and B show the SEM images of the monoliths prior and after coating with the support. The uniformity of the synthetic TiO_2 coated on the monoliths, observed in the cross-sectional view of monolith in Fig. 5 C, can be attributed to the good adhesion of the coated TiO_2 . The good adhesion and lack of excessive cracks under the reaction conditions is desirable in preventing the possibility of support loss and loss of active metal due to thermal stress at high temperatures.

The reduction behavior of Cu/X-TiO₂ (X = La, Zn, Sm, Ce) and Cu/ Sigma-TiO₂ catalysts were found using the TPR analysis (Fig. 6). It must be pointed out that all of the catalyst TPR peaks consist of two reduction regions. In fact, the first region at lower temperatures corresponds to CuO, which have weak interactions with the support while those at higher temperatures are attributed to CuO on the surface of TiO₂. Zhou et.al [48] divided the TPR curve of the catalyst to five parts (α_1 , α_2 and β for temperatures less than 300 °C and γ_1 and γ_2 for temperatures higher than 300 °C) in which the first three parts belong to high disperse particles and the others to the bulk CuO. They concluded that by increasing the dispersion of copper oxide, reduction temperature decreases considerably, however the free copper oxide reduction takes place at temperatures higher than 350 °C. According to the results of the TPR analysis, the addition of Ce promoter considerably decreases the reduction temperature of Cu/Ce-TiO₂ catalyst compared with the catalyst without promoter. This decrease is slight in the case of Zn and Sm promoters. However, the addition of La promoter to TiO₂ support increases the reduction temperature of Cu/TiO₂. Therefore, the addition of these promoters affects the interaction between the CuO and TiO₂ support remarkably.

Increasing copper oxide distribution on the support decreases the reduction temperature [48]. Therefore, the positive effect of the support can be well realized according to the TPR of CuO since CuO reaches maximum reduction at 235 °C in the absence of the support. However, CuO impregnated on the support is reduced below 200 °C. In



Fig. 6. TPR curves of Cu/Ce-TiO2, Cu/La-TiO2, Cu /Sm-TiO2 and Cu /Zn-TiO2 in the left side and Cu/TiO2 (Sigma), Cu/TiO2(Sinthesis) and CuO bulk in the right side.

Table 3 Reactor tests of Cu/TiO₂ support in light and dark condition.

Catalyst	Temperature (°C)	Conversion dark (%)	Conversion light (%)	Growth of conversion Δ^1	H ₂ Selectivity dark (%)	H ₂ Selectivity light (%)	CO Selectivity dark (%)	CO Selectivity light (%)
Cu/TiO ₂ (Sigma)	150	25.8	37.6	11.8	47.4	54.6	6.3	7.6
	200	37.2	46.5		52.8	56.8	7.5	9.0
Cu/TiO ₂ (Synthetic)	150	44.9	60.9	16	76.3	94.2	4.4	5.2
	200	74.5	87.3		80.7	95.5	5.5	6.5
Cu/Zn-TiO ₂	150	35.1	52.2	17.1	74.0	86.3	0.5	0.9
	200	62.8	76.7		76.9	86.4	0.7	1.0
Cu/La-TiO ₂	150	42.7	61.5	18.8	81.5	94.2	5.7	6.4
	200	72.3	86.5		84.8	95.5	6.7	7.5
Cu/Ce-TiO ₂	150	36.8	56.9	20.1	78.6	91.6	1.1	1.7
	200	70.4	85.7		83.6	95.0	1.4	1.9
Cu/Sm-TiO ₂	150	40.6	63.1	22.5	85.6	98.8	0.6	0.9
	200	66.2	83.8		81.9	94.4	0.9	1.1

1: Δ = conversion in light-conversion in dark.

Reaction conditions: WHSV = $8.5 h^{-1}$, H₂O/MeOH = 1, p = 0.1 MPa.

other words, the presence of the support considerably helps the distribution of copper metal, which increases the catalytic activity. What must be emphasized on is the low reduction temperature of the copper oxide on the synthetic support compared with that impregnated on the sigma support. As indicated, this results in enhanced catalytic activity due to the increased distribution of copper oxide.

3.2. Hybrid photo-thermal-catalytic activity

To investigate the synergic effect of heat and light in methanol reforming reactions, the reactor tests were performed in the dark and under light conditions with a hybrid photo-thermal-catalyst (Cu/TiO₂/ monolith). To design proper conditions, the light source (LED lamps with range 380-700 nm) [49] were placed on top of the reactor, while the reactor, heater and light source were covered with aluminum foils. The obtained results for this investigation are summarized in Table 3. Accordingly, the light treatment improves the methanol conversion by about 36 % (((conversion in light - conversion in dark)/ conversion in dark)*100) in low temperatures (150 °C). Fundamentally, the light irradiation enhances photo-excitation processes, which induces charge separation through the different parts of the catalyst (Cu, CuO, Cu₂O and TiO₂). The TiO₂ nanoparticles, an n-type semiconductor, could act as the photo-excited ingredient, charge carrier or both of them in the photocatalytic reaction. Thus, these photocatalytic properties and physical

properties (such as porosity) of the TiO_2 nanoparticles can be the reason for the observed synergism between heat and light. Also, for each detected carbon source (such as CO_2), three molecules of hydrogen have been generated indicating a similar mechanism to SRM pathway. Besides, the CO selectivity had few changes in the presence of light compared with dark conditions. It seems, the CO selectivity is less sensitive to charge separation on the TiO_2 catalyst.

To gain further insight into the role of TiO_2 in reforming methanol, the performance of Cu/doped-TiO₂/monolith in dark and light conditions were studied. Methanol conversion, H₂ selectivity and CO selectivity of samples in dark conditions are displayed in Fig. 7. Also, the performance of these catalysts in the presence of light are summarized in Table 3 and compared with dark conditions. Accordingly, methanol conversion and H₂ selectivity of all samples were increased in the presence of light. Also, methanol conversion increased when raising the temperature, which can obviously be attributed to the endothermic nature of the SRM reaction [50]. Moreover, the observed data indicates that the synthesized TiO₂ supports yield better conversion compared with the commercial ones. This outcome can be clearly interpreted by the appropriate surface area in the synthesized supports, which improves the surface contact between the catalysts and reagents (see BET data in Table 1). In low temperature tests (150 °C), the conversion of synthesized catalysts (both dark and light condition) shows a trend (pure TiO₂, La > Sm > Ce > Zn) similar to the trend of the observed density of localized states and resistance of the TiO₂ (Table 2). It could be related to this fact that the transition of rare earth electrons led to the enforcement of the photo adsorption of catalyst and supported the separation of photo generated electron-hole pars. Also, the red shift of Titania by rare earth ion doped, was helpful to the improvement of visible photo catalytic activity of TiO₂ [51,52].So, the question is: How electron and density of localized states affect the methanol-reforming reaction. In the SRM reaction, the methoxy dehydrogenation step is the rate-determining step (RDS) of the reaction [53]. This step in the photocatalytic reforming of methanol (without heat) is catalyzed by light irradiation, which produces holes and electrons in TiO₂. The holes are placed at the valance band of TiO₂ and the electrons are transferred from CB of TiO₂ to the metal particles [54]. In that case, the carbon oxidation step occurs on the metal particles or at the metal/TiO2 interface while water reduction occurs on the TiO₂ [55]. In this situation, the methoxy dehydrogenation step is catalyzed by accumulated electrons in metal particles and the reaction is achieved with UV irradiation (photocatalytic reaction) at room temperature. It seems a mechanism. which is similar to the photocatalytic reforming of methanol, plays an important role in the hybrid photo-thermal-catalytic reforming of methanol. N-type semiconductors such as ZnO and TiO₂ (as supports in MSR) [50,56] are the source of electrons. These electrons could be produced by light irradiation and/or come from defects of the semiconductors. Also, electrons transfer through the TiO₂ layer with trapping-detrapping of electrons between conduction band and localized state of TiO_2 [57]. Due to the placement of the work function of Cu (-4.7 eV) under the CB of the TiO2 (-4.2 eV), the electrons are transferred from CB of TiO₂ to Cu particles [58]. Furthermore, the transfer of electrons in the reverse direction (from Cu to TiO₂) is inhibited by a Mott-Schottky barrier. The holes can remain in the TiO₂ valance band or transfer to the copper oxides (copper particle partially oxidized at SRM reaction) [59].

Fig. S7, Shows the both CuO and Cu₂O are p-type semiconductors and can accept holes from TiO₂ [60]. Besides, the copper oxides can absorb light and produce electrons, which can transfer to the TiO₂ conduction band or directly to Cu particles. Therefore, TiO₂ is a source and carrier for the electrons and holes. Fig. 8, shows the schematic representation of electron and hole transfer between copper oxide, copper and TiO₂. Thus, a light source enhanced the methanol conversion by injecting electron to copper catalyst and facilitating the methoxy dehydrogenation process, which is the RDS of the reaction. Developing localized states of TiO₂ film and/or reducing its resistance improves electron transfers resulting in the enhancement of the methanol conversion (please see reactor test and CV results of pure TiO₂ and La doped sample).



Fig. 7. Conversion and product selectivity, (a) methanol conversion, (b) H_2 selectivity, and (c) CO selectivity with a feed WHSV = 8.5 h⁻¹ using the different nanocatalysts in the dark condition.



Fig. 8. Scheme of electron and hole transfer between the copper oxide.

All the synthesized samples have appropriate H_2 selectivity, which is better compared with commercial TiO₂ (Fig. 7b and Table 3). Also, the obtained data indicates that the presence of Zn and lanthanides improves H_2 selectivity. The CO selectivity of samples is displayed in Fig. 7c and Table 3. The observed trend of CO selectivity is similar to that of the surface states traps (see CV results).

The presence of Sm, Zn and Ce doping agents in TiO_2 structure increases its photocatalytic activity [61–63]. This can be attributed to the increased surface defect in TiO_2 structure. In other words, Sm, Zn and Ce doping agents cause oxygen vacancy, which is a kind of surface defect in TiO_2 structure. The presence of surface vacancies increases surface oxygen, which considerably helps the hydration reaction (1) [61,64]. Accordingly, reactions 3, 4 and 5, which are parts of water gas shift reaction, are facilitated leading to reduced CO content.

It must be pointed out that Ce is highly capable in oxygen mobility [65–67]. Thus, by forming oxygen vacancies, a large quantity of oxygen becomes available to Ce for oxygen mobility. Therefore, Co content considerably decreases due to high rate of water gas shift reaction, compared with other doping agents (Fig. 7c).

$$V_o + H_2 O + O_o^x \rightarrow 2 O H_o \tag{1}$$

These traps can play important roles in the water gas shift (WGS) reaction:

$$H_2O + CO \rightarrow CO_2 + H_2 \tag{2}$$

The reaction pathway involves the following steps:

$$H_2O_{ads} \rightarrow OH_{ads} + H_{ads}$$
 (3)

$$CO_{ads} + OH_{ads} \rightarrow OCOH_{ads}$$
 (4)

$$OCOH_{ads} + H_{ads} \rightarrow CO_{2 gas} + H_{2 gas}$$
(5)

Although strong interactions between the surface traps of TiO_2 and CO was observed, it is important to note that neither TiO_2 particles nor Cu particles are inactive in the WGS reaction [68]. On the other hand, H₂O can readily dissociate on the surface traps (O vacancies) of TiO_2 , which is the rate-determining step of the WGS reaction [59,69]. Furthermore, these traps improve the dispersion of Cu particles on the TiO_2 surface [70]. For instance, developing surface traps in the Ce and Sm samples improved the surface area of these samples compared with other samples (please see the BET results). According to the literature, the adsorption and dissociation of H₂O probably takes place on TiO_2 , while CO adsorbs on the copper nanoparticles and all the subsequent reactions occur at the metal oxide/copper interface [28]. Consequently, the appropriate CO selectivity of Zn, Sm and Ce doped samples is explained by the development of the Surface state traps (H₂O dissociation sites) and improvement of the Cu/TiO₂ interface.

To further investigate the effects of the TiO_2 defects on the methanol reforming reaction, a catalyst support with a high concentration of TiO_2 defects was designed. Hence, synthesized alumina with a suitable surface area (BET about $350 \text{ m}^2/\text{gr}$) was treated with a $TiCl_4$ solution

Table 4

The reactor test of alumina/ Tio	0 ₂ , TiO ₂	and alumina	supports in SF	M reaction	(Reaction conditions:	WHSV	$= 8.5 h^{-1}$	¹ , H ₂ O/MeOH :	= 1, p	=0.1 MPa).
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Support	Temperature (°C)	Conversion (%)	CO selectivity (%)	BET Surface area(m ² /g)
Cu/Alumina/TiO ₂	200	28.8	0.0	40.2
Cu/TiO ₂	200	69.6	6.8	76.7
Cu/Alumina	200	50.38	9.7	63.5



Fig. 9. TGA analysis of Cu/X-TiO₂ (X = Sm, La, Ce, Zn) under air of used catalysts during 56 h' time on the stream reaction at 250 °C.

(2 mM for 10 min in 70 °C). With this treatment method, a thin layer of dense and amorphous TiO2 was deposited on the Alumina surface [71,72]. The electronic resistance of this support is considerably increased due to the thinness of the TiO₂ layer and the high electronic resistance of the alumina. However, the surface defect of this sample increased due to the increasing ratio of the interface-TiO₂/bulk-TiO₂ and amorphous structure of the TiO₂. The mesoporous structure of the alumina improves the TiO₂ and alumina interfaces, which increase interface defects. The elemental mapping of this support was investigated by EDX dot mapping analysis and resulting data were displayed in Fig. S6. So, individual mapping of the Ti element indicated appropriate dispersion of this element on the alumina surface. Also, the quantitative analysis of the EDS spectra indicates that the weight percentage of the Ti is about 0.1 percent. Table 4 shows the obtained reactor test for this support in a fixed-bed reactor and dark conditions. The obtained results indicated that CO selectivity is more favorable in the alumina/TiO₂ sample (0.0 %) compared with other supports. This result confirms the outcomes of the doped-TiO₂ reactor tests, in which the TiO₂ surface defects improve the CO selectivity. Furthermore, methanol conversion was reduced in the alumina/TiO2 sample compared with TiO2 and alumina samples. This can be explained by the lower surface area of the alumina/TiO2 sample compared with the alumina sample and the higher electronic resistance of this sample compared with TiO₂, respectively.

To evaluate the coke formation and its amount on the used Cu/X-TiO₂ (X = Sm, La, Ce, Zn) nanocatalysts (56 h in the methanol steam reforming conditions at 250 °C and atmospheric pressure), TGA analysis was carried out. The results are displayed in Fig. 9. Based on the TGA results, the order of the coke formation resistance of Cu/X-TiO₂ samples (X = Sm, La, Ce, Zn) is as follows: Sm < Zn < Ce < La. To note, the presence of Sm and Zn promoters in the catalyst structure considerably decreases coke formation. However, coke formation was enhanced about two times in the Cu/La-TiO₂ sample compared with Cu/Sm-TiO₂ and Cu/Zn-TiO₂ samples. Accordingly, Sm-doped TiO₂ presented advantages such as high conversion, low-temperature reactivity, high CO₂

selectivity and high resistance toward coke formation.

4. Conclusions

In this work, the synergistic effect of light and heat in methanolreforming over hybrid photo-thermal catalysts (Cu/TiO₂/monolith) were investigated. According to the reactor tests, it has been revealed that hybrid photo-thermal catalysts are effective catalysts for methanolreforming in low-temperature conditions. Particularly, the methanol conversion was increased by about 36 % due to irradiation from a weak light source (80 lx). Considering the important role of TiO₂ nanoparticles as catalyst supports in this synergism, the properties of the TiO₂ nanoparticles were modified with metal doping to study the effects of TiO_2 in this reaction. The dopants effects were investigated by cyclic voltammetry analyses, indicating dopants change the density states (DOS), electrical resistance and surface state traps of TiO₂ nanoparticles. Among them, density states (DOS) and resistances which are important in electron transfer through the catalyst, impact methanol conversion. For instance, higher DOS and lower resistance in the La-doped sample compared with the Zn-doped sample improve methanol conversion by about 23 %.

Also, samples with high surface state traps enhanced the CO selectivity of the reaction. The surface state traps reduced the CO content in the Zn-doped sample (2.0 %) compared with the pure TiO₂ sample (8 %). This effect was evaluated by preparing an alumina/TiO₂ support, developing TiO₂ surface defects. The observed reactor test indicated that the CO selectivity was completely enhanced for the alumina/TiO₂ support (0.0 %) compared with TiO₂ support (6.8 %). Consequently, increasing light absorption and charge separation through the hybrid photo-thermal catalysts enhance methanol conversion, while improving the surface state traps of TiO₂ enhances the CO selectivity of the reaction.

CRediT authorship contribution statement

Yasin Khani: Methodology, Writing - original draft, Visualization, Data curation. Pooya Tahay: Methodology, Data curation, Visualization, Writing - original draft. Farzad Bahadoran: Supervision, Conceptualization, Investigation, Writing - review & editing. Nasser Safari: Supervision, Investigation. Saeed Soltanali: Software, Validation. Ali Alavi: Resources, Validation.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2020.117456.

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