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REVIEW

Influence of nanocatalyst on oxidative coupling, steam and dry reforming of methane: A short review



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Abstract The influence of nanocatalyst on three main reactions for natural gas conversion such as steam reforming, dry reforming and oxidative coupling of methane has been reviewed with an emphasis on the literatures' reports and results. Although literatures' experimental results showed that the conversion of methane over the nanocatalysts was higher than that obtained from the ordinary catalysts, there was no correlation between the conversion of methane and the average sizes of the nanoparticles. The results of some nanocatalyst are also compared to ordinary catalysts in the literature which shows the improved influence of nanoscale catalyst performance on methane conversion.

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1. Introduction

Although methane is an excellent raw material for the production of fuels and chemicals, the main use is as fuel for power generation and for domestic and industrial uses. Large amounts of methane are found in regions that are located far away from industrial complexes and often methane is found off shore. This means its transportation is uneconomical or



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even impossible. Therefore, parts of the methane obtained, is re-injected, flared or vented at the moment, which is waste of hydrocarbon resource (Farsi et al., 2010; Lunsford, 2000).

On the other hand, both methane and CO₂ are greenhouse gases responsible for global warming and more strict regulations about letting out or flaring are expected in the future (Lunsford, 2000). These transportation and environmental problems and the increasing oil price have led to world-wide efforts for converting methane into easy transportable value added products, such as ethylene, aromatics and liquid hydrocarbon fuels (Amenomiya, 1990; Ross et al., 1996). Methane can be converted into chemicals and fuels in two ways, either via synthesis gas or directly into C₂ hydrocarbons or methanol (Farsi et al., 2010; Lunsford, 2000; Amenomiya, 1990; Ross et al., 1996). For instance, concerning global warning issues both methane and CO₂ can convert greenhouse gases into synthesis gas by dry reforming which is an important feedstock for many industrial processes (Hu, 2010; Xu and Wei et al., 2003; Xu et al., 2003).

Recently, nanocatalysts have attracted much attraction (Shu et al., 2007). In comparison with their micro-sized counterparts, nanocatalysts show higher activity, better selectivity, and outstanding stability because of their large specific surface area, high percentage of surface atoms and special crystal structures (Farsi et al., 2011a; Guo et al., 2000). Nanoparticles can be synthesized by several methods such as sol-gel processing, micro-emulsion, homogeneous precipitation, gas evaporation, laser vaporization, ionized beam deposition, freeze drying and etc (Farsi et al., 2011a; Guo et al., 2000; He et al., 2004a).

The objective of the present review is to provide a tangible account of methane conversion over nano scale catalysts by three reactions namely as steam reforming of methane, dry reforming of methane and oxidative coupling of methane. It is intended that this review provides necessary background information and general direction to those who are involved or about to be involved in this research field.

2. Steam reforming of methane (SRM)

SRM (e.g., CH₄ + H₂O ↔ CO + 3H₂) is a crucial reaction for the production of synthesis gas (Lunsford, 2000). The process is also important for the direct electrochemical conversion of hydrocarbons in solid oxide fuel cells (SOFCs). SOFCs are a very attractive option for electrical power generation in stationary, mobile, and portable applications (Oha et al., 2003; Wu et al., 2009). Commercial catalyst for this reaction is Ni supported on a metal oxide (Wu et al., 2009; Maluf and Assaf, 2009).

The process is run under a wide range of conditions with operating temperatures from approximately 500 to 950 °C (Zhou et al., 2008). One of the critical problems with long-term performance of Ni catalysts is the formation of carbon deposits on the catalyst surface, which evolve into carbon filaments, ultimately diminishing the performance of the catalyst (Wu et al., 2009; Maluf and Assaf, 2009; Zhou et al., 2008). Three main reactions take place as in the following equations:



Both the water-gas shift reaction (Eq. (2)) and reverse methanation (Eq. (3)) are always associated with catalytic SRM at elevated temperatures. Due to their overall high endothermic nature, these reactions are carried out at high temperature to achieve high conversions.

From thermodynamics and reaction engineering perspective, SRM is a highly endothermic process and therefore demands an efficient heat supply to the system. It is usually operated in a temperature range of 700–900 °C to achieve high conversions. It is a very energy consuming and capital-intensive process although the present technology approaches 90% of the maximum thermodynamic efficiency. Although this thermodynamic and kinetic limitation is the opposite of main challenge that occurs for exothermic reactions, further research can be directed to predict a novel strategy for methane activation to produce more substances that are valuable by solving both problems of endothermic and exothermic reactions that designate (Farsi et al., 2011b).

Commercial catalysts for the SRM reaction are Ni on supports, such as Al₂O₃, MgO, MgAl₂O₄ or their mixtures (Maluf and Assaf, 2009). Selection of a support material is an important issue as it has been evident that metal catalysts are not very active for the SRM when supported on inert oxides (Sadykov et al., 2009).

Watanabe et al. (2007) studied on nanosized Ni particles. They supported Nickel nanoparticulate catalysts on hollow Al₂O₃ ball by spraying a mixed solution of Nickel and aluminum nitrates. Their solution-spraying plasma (SSP) system is shown in Fig. 1. Their system consists of: (1) an ultrasonic mist generator for a catalyst source solution, (2) a plasma torch reactor and (3) a catalyst particle collector with a water shower supplied by a circulatory pump. They used a fixed bed quartz tubular reactor for SRM. They reported a 92% methane conversion for their nanocatalyst.

Roh et al. (2007) studied highly active and stable nanosized Ni/MgO–Al₂O₃ catalyst. They concluded that the high activity and stability are due to beneficial effects of MgO such as enhanced steam adsorption, basic property, nanosized NiO, crystallite size and strong interaction between Ni and support.

Sadykov et al. (2009) studied on nanocomposite catalysts for SRM. Nanocomposite catalysts comprised of Ni particles embedded into the complex oxide matrix comprised of Y or Sc-stabilized Zr (YSZ, ScSZ) combined with doped ceria-zirconia oxides or La–Pr–Mn–Cr–O perovskite and promoted by Pt, Pd or Ru were synthesized via different routes.

3. Dry reforming of methane (DRM)

The CO₂/CH₄ reforming has been studied over numerous supported metal catalysts, such as Ni-based and noble metal catalysts (Luna and Iriarte, 2008; Zhao et al., 2008; Gallego et al., 2008; Liu et al., 2009). The DRM reaction (Eq. (4)) is accompanied by several side reactions, of which the reverse water gas shift reaction (Eq. (5)), the methane cracking reaction (Eq. (6)) and the Boudouard reaction (Eq. (7)) appear to be the most important:



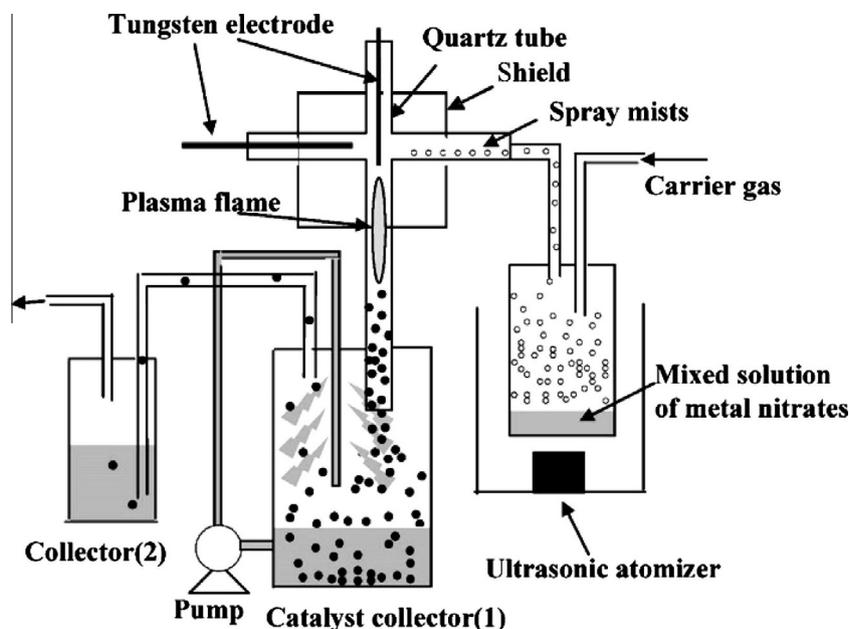


Figure 1 Solution-spraying plasma system for the preparation of nano sized catalysts on hollow oxide balls.



In many literatures (Zhao et al., 2008; Gallego et al., 2008; Liu et al., 2009; Kroll et al., 1996; Steinhauer et al., 2009), rare earth oxides are usually added to the nickel-based catalysts for CO_2/CH_4 reforming as a promoter to optimize the activity of the catalysts. However, performing DRM with traditionally prepared nanoparticle catalysts such as Ni nanoparticles has met with several severe obstacles.

One of the current constraints in DRM is about surface analysis which has been studied less than the catalyst synthesis and characterization investigations. To address this constraint, Kiennemann and co-workers used spinel and perovskite support (Parvary et al., 2001; Djaidja et al., 2006; Sahli et al., 2006; Valderrama et al., 2005). The effect of Ni/Al ratio on the structure of NiAl_2O_4 spinel was suggested as an important factor related to small metallic particles to obtain a good performance for the reforming of methane into synthesis gas with limited coke formation. They reported that the growing of the Ni particles needs to be limited. The author found that NiMg/ Al_2O_3 catalysts, prepared by co-precipitation method and Ni/MgO, prepared by impregnation, are suitable catalysts for selective DRM. The catalysts are remarkably active even at the lowest reaction temperature studied (700 °C) showing a low carbon deposition even at the highest reaction temperature (850 °C). A previous reduction of the solids improves their catalytic activity. Their results revealed that the catalytic behavior of these catalysts could be explained in terms of the reducibility and also of the good dispersion of Ni species due to the interactions between Ni and Mg–Al.

Gonzalez-Delacruz et al. (2011) worked on the effect of a reduction process with CO or H_2 on the size of nickel particles in Ni/ ZrO_2 DRM catalysts. Their results signify that a high temperature treatment with CO increases the dispersion of

the nickel metallic phase. Their X-ray Absorption Spectroscopy results have shown a lower coordination number of Ni in the sample treated with CO than that reduced with H_2 . They also showed that under the CO treatment, the formation of $\text{Ni}(\text{CO})_4$ complexes corrodes the nickel particles, decreasing their size. The formation of these gas molecules occurs without measurable losses of nickel from the catalyst which maintains the same nickel content after the hydrogen or the CO treatment at high temperature. They concluded that different effects of CO on nickel catalysts have been formerly described, though they have found for the first time more than a few experimental evidences demonstrating the whole re-dispersion phenomenon.

Qu et al. (2008) studied the catalytic reaction of CO_2 reforming of methane using Ni/CO nanoparticles which are believed to be immobilized at the tips of single-walled carbon nanotubes (SWNTs). Their results revealed that (1) SWNTs are a better support for nanocatalysts at high temperatures; (2) nanoparticles at the tips of SWNTs are small enough to reduce or even eliminate carbon deposition on them; and (3) nanoparticles at the tips of SWNTs do not sinter during DRM.

Rezaei et al. (2008) studied DRM over nanocrystalline zirconia-supported nickel catalysts. They prepared nickel catalysts by excess-solution impregnation using zirconia powder and an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The best methane conversion of their catalyst was 70%.

The nanocatalysts performance results such as BET surface area of catalyst, reaction temperature, feed portions and methane conversion are compared to relevant works on ordinary catalysts for SRM and DRM reported in Table 1. Many works (Shu et al., 2007; Aiken and Finke, 1999; Trionfetti et al., 2006) show that preparation of a catalyst with high surface area has a great effect on its properties, and this can be attained by a nanocatalyst. This advantage is in contrast with those of the ordinary catalysts with similar combinations. These effects

Table 1 Comparison between ordinary catalysts and nanocatalysts on SRM and DRM.

<i>T</i> (°C)	Catalyst	BET (m ² /g)	CH ₄ :H ₂ O:CO ₂	% Methane conv.
700	Ni/Ce–ZrO ₂ /θ-Al ₂ O ₃ (Farsi et al., 2011)	167	1:3:0	97
800	Ni/NiAl ₂ O ₄ /γ-Al ₂ O ₃ (Oha et al., 2003)	148.3	1:3:0	60–98
750	Ni–Al ₂ O ₃ (Sadykov et al., 2009) ^a	209	1:0:1	85
700	Ir/Al ₂ O ₃ (Wang and Gorte, 2002)	2.268	1:0:1	48–67
700	La ₂ NiO ₄ (Watanabe et al., 2007)	11	1:0:1	81–85
850	Ni–MCM-4 (Roh et al., 2007)	0.71	1:0:1	99
700	Ni–Pd/(ZrO ₂ –La ₂ O ₃) (Zhao et al., 2008) ^a	96	5:0:4.5	73
700	Ni/Al/Mo (He et al., 2004)	97.7	4:1:0	98
750	Pt/Pr _{0.3} Ce _{0.35} Zr _{0.35} O ₂ /Ni/YSZ (Wu et al., 2009) ^a		1:3:0	91
700	Ni/SBA–15/ZrO ₂ /Al ₂ O ₃ /FeCrAl (Guo et al., 2000)		1:2:0	96–98
750	Ni/CeO ₂ –Al ₂ O ₃ (Valderrama et al., 2005)	127.2	1:0:1	88
700	Ni/(NiK ₂ O/ZrO ₂) (Gonzalez-Delacruz et al., 2011) ^a	174	1:0:1	75
700	Ni/CaO (Qu et al., 2008)	15.2	1:0:1	52
700	Nickel/Zirconia (Liu et al., 2009) ^a	134.67	1:0:1	64.12
800	LaRu _{0.8} Ni _{0.2} O ₃ (Rezaei et al., 2008)	9	1:0:1	78.6
800	La _{0.8} Ca _{0.2} Ru _{0.8} Ni _{0.2} O ₃ (Rezaei et al., 2008)	3	1:0:1	98.5
700	Ni–Ti (Aiken and Finke, 1999)	1.9	1.8:0:1	30–40
700	Ni–Al–Ti (Aiken and Finke, 1999)	86.4	1.8:0:1	67.5

^a Denotes to a nanocatalyst.

can alter the reaction parameters, sometimes on conversion. Comparing nanocatalysts with their corresponding ordinary catalysts shows that these improvements can not only alter conversion, but also the other parameters. These alterations are merely for the nanocatalyst and its corresponding catalyst with identical combinations. This is clear that two catalysts with different properties cannot be thoroughly compared by just considering their scale. This has to be noted that it is perfectly apparent that the catalysts and nanocatalyst presented in Table 1 have been characterized in various reaction conditions such as temperature, feed portions, reactor geometry and type of the reactor.

4. Oxidative coupling of methane (OCM)

The normally accepted scheme for OCM is as follow (Farsi et al., 2010; Farsi et al., 2011a,c). The principal reactions are



and the main unwanted reactions are:



Due to the above scheme, methane is first partially oxidized to ethane in reaction 8. A secondary reaction of oxydehydrogenation of ethane then proceeds to form ethylene in reaction 9. Two further steps are the nonselective oxidation of methane to carbon dioxide and carbon monoxide (reactions 10 and 11).

The challenges that limit the commercialization of OCM process are: (I) high temperature (700–900 °C) to achieve high ethylene and ethane (C₂₊) yield; (II) The active sites in the coupling catalysts activate also the C–H bond in C₂₊, resulting in the formation of CO₂ by combustion; (III) limitation on methane conversion (<45%) and C₂₊ yield (<27%) imposed

by the explosion limit of oxygen concentrations in the feed; (IV) low concentrations of ethylene in the product, making the separation of the product stream uneconomical; (V) low selectivity at higher conversion, making the achievement of simultaneous good selectivity and conversion extremely difficult (Sinev et al., 2009; Choudhary and Uphade, 2004; Sekine et al., 2009). Some of these problems can be overcome by the use of nanocatalyst.

A series of nanocatalysts for the OCM based on MgO with a varying content of Li have been synthesized. Farsi et al. (2011a) prepared Li/MgO catalyst and nanocatalyst by the incipient wetness impregnation and sol–gel method, respectively. Their catalyst and nanocatalyst were tested at wide range of temperature (700–800 °C) at constant total pressure (~1 atm). Their results show that using Li/MgO nanocatalyst in the OCM would result in higher conversion of methane, higher selectivity and higher yield of C₂₊ hydrocarbons compared to ordinary catalyst. Their results of methane conversions in OCM reaction over Li/MgO ordinary and nanocatalyst in different range of temperature and CH₄/O₂ are illustrated in Fig. 2(a) and (b), respectively. Due to these figures the conversion of methane by the Li/MgO nanocatalyst was apparently higher than ordinary catalyst especially at higher temperatures.

In another work on Li/MgO nanocatalyst, morphology and microstructure of this nanocatalyst were investigated by Zavyalova et al. (2011) in OCM reaction. They asserted that the resulting catalytically active systems are studied by a combination of TEM and SEM methods. Samples with a low profusion of Li reveal a hierarchical pore system built from tubular structures made from primary MgO particles. Morphological indications have been established for the role of Li as flux in this transformation. The alteration of the primary particle morphology leads to a drastic change in secondary structure from open sponges to compact sintered plates. They also showed that a relation was found between catalytic function in OCM and the transformation from cubic to complex-terminated particles. They concluded that, it is suggested that

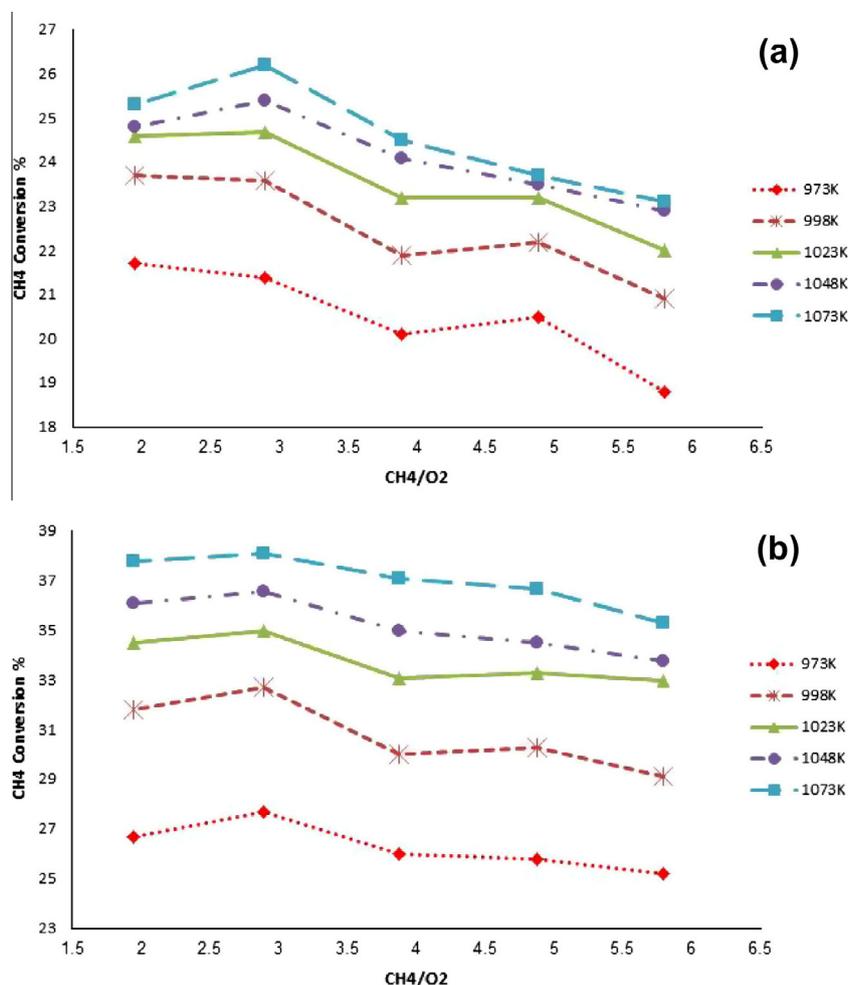


Figure 2 Profile of percent of methane conversion versus CH_4/O_2 over Li/MgO at different feed temperatures: (a) ordinary catalyst, (b) nanocatalyst.

sites active for the coupling reaction of methane are related to the projections arising from segregation of oxygen vacancies to the surface of MgO.

He et al. (2004b) synthesized and tested the CeO_2/ZnO nanocatalysts performance on the OCM with carbon dioxide as an oxidant. They prepared this catalyst using a novel combination of homogeneous precipitation with micro emulsion. The prepared catalyst was compared with those prepared using a conventional impregnation. Fig. 3 shows TEM images of CeO_2/ZnO nanocatalyst and CeO_2/ZnO catalyst prepared by the conventional impregnation. They concluded that a better low temperature activity has been achieved over the nanocatalyst, but there was no regular relationship between the average size of nanocatalyst and their catalytic performance. However, the conversion of methane increased by increasing fractal dimension of CeO_2/ZnO nanocatalyst.

He et al. (2003) also synthesized $\text{La}_2\text{O}_3/\text{BaCO}_3$ nanocatalyst for OCM with CO_2 as oxidant. Their nanocatalyst was synthesized by coupling route of homogeneous precipitation with micro emulsion under pulsed microwave heating; and compared it with $\text{La}_2\text{O}_3/\text{BaCO}_3$ ordinary catalyst which was prepared by conventional homogenous precipitation. Their results showed

that in case of the nanocatalyst, the oxidative coupling can take place at 100°C lower than the startup temperature over the conventional catalysts. They concluded that the conversion of methane is higher in reaction with nanocatalyst but the improvement of C_{2+} selectivity was not distinct and the carbon deposition on the nanocatalyst was more serious.

In addition to the previously mentioned features of the nanocatalyst over OCM before in this work, The nanocatalysts performance results such as method of preparations, feed portions, methane conversion and C_{2+} selectivity and yields for OCM reaction are compared with ordinary catalyst and reported in Table 2.

The kinetics of OCM reaction which produces C_{2+} has been studied extensively based on various reaction mechanisms. Former researches have shown that the kinetics of OCM reaction is very complicated in terms of the proposed mechanisms since they involve several chemical species. In spite of the extensive research done on kinetics of OCM reaction during past thirty years, there are very few reports addressing the kinetics of OCM reaction over the nanocatalysts. Amongst the few works that are available in the literature, Farsi et al. (2011c) investigated the kinetics of OCM

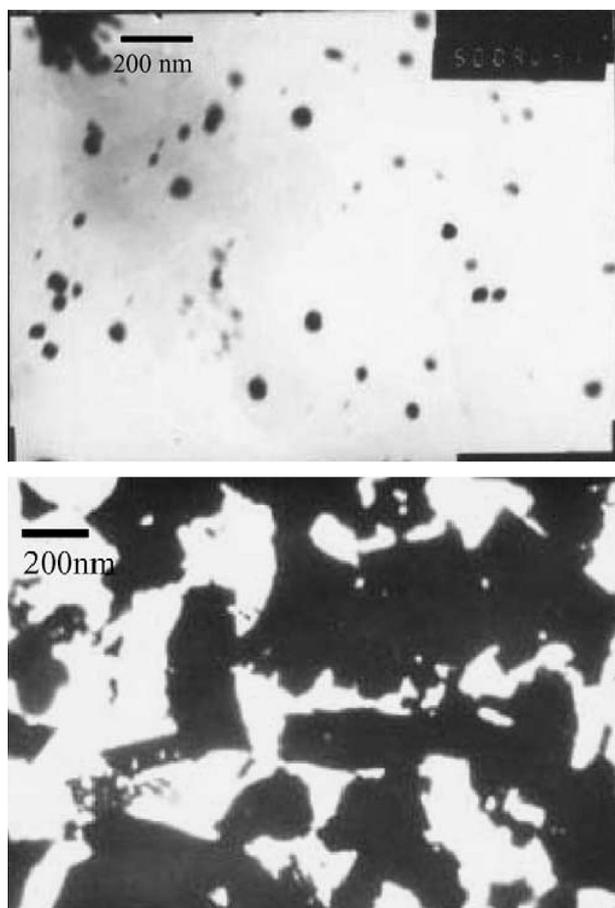


Figure 3 TEM images of CeO₂/ZnO nanocatalyst prepared by the combining method (top) and ordinary catalysts prepared by the conventional impregnation (bottom).

over La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ} nanocatalyst which was synthesized by citric-EDTA complexation method. The goal of their work was to propose and discuss a simple power law kinetic model which may assist the researchers in computer aided designs and reactor simulations. They claimed that it can be useful for estimating the methane conversion, and C₂₊ selectivity and yield under the considered conditions. In order to propose a simple kinetic model over above mentioned nanocatalyst, they surveyed the available mechanisms and four reaction steps were chosen in which the most important reactions are leading to OCM products and common among all the available mechanisms. The accuracy of the kinetic model was evaluated by its ability to predict experimental data. Their results showed that the power law model can be used for kinetic modeling of OCM. From this point of view, their model may be used as a generic one for OCM nanocatalysts with similar properties.

5. Conclusion

Regardless the type of catalyst used for the SRM, DRM and OCM the achievements of high stability and high catalytic activity low temperatures are the main targets to attain. The increasing research on nanocatalysts is resulting in the production of new and efficient nanocatalysts with promising results. In this study, the catalytic performance of the nanocatalysts on SRM, DRM and OCM was reviewed and compared to ordinary catalysts. Using nanocatalyst, the conversion of methane, C₂₊ selectivity and main products yield in many cases were higher compared to the ordinary catalyst. Due to comparing the result of nanocatalysts with other ordinary catalysts which is given in the literature, the effect of nanocatalyst on catalyst activity is elucidated to some extent.

Table 2 Comparison between OCM ordinary catalysts and nanocatalysts.

T (°C)	Catalyst	Method of preparation	CH ₄ /O ₂ or CO ₂ %	C ₂ Yield %	C ₂ Selec. %	CH ₄ Conv.
800	CeO ₂ /ZnO (Kroll et al., 1996)	Combination of homogeneous precipitation with micro-emulsion	1/2 with CO ₂		81	0.5
800	CeO ₂ /ZnO ^a (Kroll et al., 1996)	The conventional impregnation	1/2 with CO ₂	4.79	83.6	5.73
800	La ₂ O ₃ /BaCO (Sahli et al., 2006)	Traditional homogeneous precipitation	1/2 with CO ₂		88	0.6
800	La ₂ O ₃ /BaCO ^a (Sahli et al., 2006)	Coupling route of homogeneous precipitation with micro emulsion under pulsed microwave heating	1/2 with CO ₂		88.5	4.5
700	NaN ₃ /MgO (Djaïdja et al., 2006)	Described in the article	16/14	14.1	52	27.1
700	LiNO ₃ /MgO (Trionfetti et al., 2006)	Described in the article	16/14	4.6	58.5	7.9
700	Li ₂ SO ₄ /MgO (Trionfetti et al., 2006)	Described in the article	16/14	1.5	72.4	2.1
800	LiNO ₃ /MgO (Trionfetti et al., 2006)	Described in the article	16/14	10.6	55.5	19.1
800	CaWO ₄ -Mn/SiO ₂ (Farsi et al., 2011)	Incipient wetness impregnation method	3.2/1	4.8	25.3	19
800	CaWO ₄ -Mn/SiO ₂ (Farsi et al., 2011)	Incipient wetness impregnation method	3.2/1	4.6	25	18.2
800	FeWO ₄ -Mn/SiO ₂ (Farsi et al., 2011)	Incipient wetness impregnation method	3.2/1	2.7	14.6	18.3
800	FeWO ₄ -Mn/SiO ₂ (Farsi et al., 2011)	Incipient wetness impregnation method	3.2/1	2.7	15.1	17.7
800	CoWO ₄ -Mn/SiO ₂ (Farsi et al., 2011)	Incipient wetness impregnation method	3.2/1	4.2	23	18.3
800	CoWO ₄ -Mn/SiO ₂ (Farsi et al., 2011)	Incipient wetness impregnation method	3.2/1	4.3	23.8	18.1
800	NiWO ₄ -Mn/SiO ₂ (Farsi et al., 2011)	Incipient wetness impregnation method	3.2/1	4.4	23.8	18.4
800	NiWO ₄ -Mn/SiO ₂ (Farsi et al., 2011)	Incipient wetness impregnation method	3.2/1	3.7	20.5	17.9
700	Li ₂ SO ₄ /La ₂ O ₃ (Sinev et al., 2009)	Described in the article	16/14	13.3	59.9	22.2
700	LiNO ₃ /La ₂ O ₃ -MgO (Sinev et al., 2009)	Described in the article	16/14	14.9	58.8	24.2
700	Li ₂ SO ₄ /La ₂ O ₃ -MgO (Sinev et al., 2009)	Described in the article	16/14	16.6	64.3	25.8

^a Denotes to a nanocatalyst.

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