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Catalytic Performances of Ni and Cu Impregnated MCM-41 and Zr-MCM-41

for Hydrogen Production Through Steam Reforming of Acetic Acid

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Graphical abstract



Highlights

- Zr-MCM-41 were synthesized successfully using a one-pot hydrothermal procedure
- Performances of Cu based catalyst are poor in terms of steam reforming reactions
- Ni-silica catalysts are highly promising in the production of hydrogen rich syngas
- Zr incorporation enhanced the activity of the Ni based MCM-41 catalyst
- Coke deposition over Ni based catalyst was decreased by Zr incorporation

Abstract

A new mesoporous catalyst support material was synthesized by incorporation of zirconia into the structure of MCM-41 through a one-pot procedure. Catalytic performances of MCM-41 and Zr incorporated MCM-41 (25Zr-MCM-41) supported Ni or Cu catalysts were investigated in steam reforming of acetic acid reaction, at 750°C. Some deformation in the ordered pore structure of MCM-41 was observed as a result of Zr incorporation. The activity test results showed that the catalytic performances of the zirconia incorporated MCM-41 were more stable than the MCM-41 supported materials. The catalysts containing 5% and 10% Ni gave highly promising results to achieve high hydrogen selectivity. However, the performance of the catalysts containing 5% Ni was more stable. Comparison of performances of Cu and Ni based catalysts showed that Cu was not a good catalyst for the steam reforming reaction of acetic acid. In the presence of copper, mainly decarboxylation reaction of acetic acid took place, yielding large quantities of methane. Results proved that, 5% Ni impregnated 25Zr-MCM-41 was a highly promising catalytic material for hydrogen production through steam reforming of acetic acid.

Keywords: Hydrogen, Acetic Acid, Steam Reforming, Copper, Nickel, Zirconia

1. Introduction

Fast increase of energy demand and the increased consumption rate of fossil resources accelerated the research activities for the development of environmentally safe alternative fuels from renewable resources. Bio-waste components are regarded as promising resources for hydrogen production. Catalytic processes for steam reforming of bio-oil components, bio-ethanol and dry reforming of bio-gas yield synthesis gas, which may then be used as a resource for the production of non-fossil fuels and valuable chemicals through Fischer-Tropsch synthesis, methanol synthesis etc [1-3]. Hydrogen is considered as an attractive clean energy carrier. While it can be produced from various raw materials, recent developments in fuel-cell technologies caused significant increase in the research and development activities for its production from renewable resources [4-7].

Flash pyrolysis of biomass (forest waste, agricultural waste, straw, industrial wood waste etc.) yields about 75-80% bio-oil, which is considered as a potential resource for the production of chemicals and/or fuels [7-10]. Catalytic steam reforming of bio-oil fractions is a potential approach to produce synthesis gas, which may then be used for the synthesis of alternative fuels or valuable chemicals. Synthesis gas produced through steam reforming of bio-oil fractions may be used as a fuel directly in solid oxide fuel cells or may be further treated to produce CO free hydrogen for PEM fuel cells.

The composition of bio-oil is quite complex and depends upon the source of biomass. As it was reported in the literature, it may contain up to 20% acetic acid. Acetic acid has been generally considered as a model compound of bio-oil for the production of synthesis gas or hydrogen [11-16]. Acetic acid (AcOH) may also be produced through fermentation of bio and fruit wastes. It is a non-toxic and non-flammable compound with quite high hydrogen content.

Steam reforming of AcOH may yield up to 4 moles of H₂ per mole of AcOH reacted (R.1). Hence, production of synthesis gas/hydrogen by steam reforming of acetic acid attracted significant attention of researchers in recent years [17-24].

$$CH_{3}COOH + 2H_{2}O \rightarrow 2CO_{2} + 4H_{2} \qquad (\Delta H^{o} = 131.4 \text{ kJ/mole})$$
(R.1)

Steam reforming of acetic acid is an endothermic reaction. Hence, it is favored at high temperatures. Product distributions of acetic acid steam reforming process indicated formation of mainly CO, CO₂, CH₄, as carbon containing compounds. Formation of some acetone was also reported in some studies. Formation of CO and CH₄ cause some decrease in hydrogen yield

from the maximum value of four per mole of AcOH reacted. Methane is formed mainly as a result of decarboxylation of AcOH (R.2).

$$CH_3COOH \rightarrow CH_4 + CO_2$$
 ($\Delta H^o = -33.5 \text{ kJ/mole}$) (R.2)

Overall stoichiometry of steam reforming of acetic acid is due to the sum of thermal decomposition of AcOH (R.3) and water gas shift reaction (WGSR) (R.4).

$$CH_3COOH \rightarrow 2CO + 2H_2 \quad (\Delta H_0 = 213.4 \text{ kJ/mole})$$
 (R.3)

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (\Delta H_0 = -41 \text{ kJ/mole})$$
 (R.4)

Water gas shift reaction (R.4) is an exothermic reaction and it is thermodynamically favored at lower temperatures. Depending upon the reaction temperature and the reaction scheme, water gas shift reaction may go through the forward or reverse directions. Methane produced through (R.2) may also further react with steam (R.5) or with CO_2 (R.6), to yield CO and H₂.

$$CH_4 + H_2O \leftrightarrow CO + 3 H_2$$
 (Steam reforming of methane) (R.5)

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$$
 (Dry reforming of methane) (R.6)

Coke formation is an undesired process which takes place during steam reforming of AcOH. Coke formation may take place through Boudouard reaction (R.7) or through dissociation of carbon containing products, like methane (R.8). Due to its exothermic nature, Boudouard reaction is favored at lower temperatures, while decomposition of methane becomes more significant at higher temperatures.

$$2CO \leftrightarrow C + CO_2 \qquad (\Delta H_o = -172.4 \text{ kJ/mole}) \qquad (R.7)$$
$$CH_4 \leftrightarrow C + 2H_2 \qquad (\Delta H_o = 74.8 \text{ kJ/mole}) \qquad (R.8)$$

Achievement of high conversions of AcOH, to obtain high hydrogen yields and to minimize coke formation is still important challenges of catalysis research. Catalytic performances of noble metals, like Pt, Pd, Ru, Rh, were reported to be quite good in steam

reforming of acetic acid [9, 21, 23, 25-28]. Results reported for the comparison of catalytic performances of noble metals and Ni based catalysts indicated that nickel was as active as noble metals, giving very high hydrogen selectivity values in steam reforming of AcOH [9]. High activity of Ni based catalysts is considered to be due to the ability of nickel to break the C-C, C-H and O-H bonds. Recent results reported with Ni and/or Co based catalysts indicated high activity for steam reforming of AcOH [13, 19, 20, 29-34]. Also, the performances of Ni-Co based bi-metallic catalysts were generally considered as being better than the mono-metallic catalysts, in terms of catalyst stability and coke minimization during steam or dry reforming reactions [3, 34-36].

Copper based catalysts were also considered quite active for some reforming reactions, like steam reforming of methanol [37, 38]. However, there are only a few studies in the literature, reporting experimental results for steam reforming of AcOH using Cu based catalysts [39-42]. In some of these studies, activities of Cu based catalysts were reported as being quite low [40, 41]. Hu et al, reported that Cu was an important metal to suppress the formation of CO, while Co was the main active metal for the reforming reaction, in the studies performed over Co-Zn-Cu, Cu-Zn, Cu-Co and Co-Zn catalysts. However, it was reported in another study on steam reforming of acetic acid that a Cu-Zn based catalyst which was supported on calcium aluminate was quite active for this reaction, giving a hydrogen yield value of 80% [42]. Clarification of these conflicting results is needed in order to have a better understanding of reaction paths over Cu and Ni based catalytic materials.

Support material of the catalysts used in reforming reactions is also expected to have significant influence on the product distributions, as well as on coke formation and catalyst stability [18, 19, 33, 43]. Different forms of alumina, zeolites, perovskites, zirconia etc. were used as the support material in many of the studies investigating steam reforming of AcOH. Discovery of the silicate structured mesoporous materials with ordered pore structures (MCM-41, SBA-15 etc.) opened new avenues for the development of new catalysts, showing less resistance for the transport of the reactants to the active sites and being less prone to deactivation due to coke formation, than the conventional microporous catalytic materials. There are limited number of publications in the literature, reporting the performances of MCM-41 type catalysts in steam reforming of alcohols and dry reforming of methane [38, 44, 45], and wood vinegar (contain 20% acetic acid) [46]. In order to improve the hydrothermal stability of silicate structured SBA-15 at high temperatures, synthesis of zirconia incorporated materials and testing of these materials as catalyst supports in reforming reactions were reported in the recent literature [47-49]. However, information about the synthesis, characterization and testing of

zirconia incorporated MCM-41 type catalyst supports is not readily available and the use of such zirconia incorporated MCM-41-like catalyst supports in reforming reactions need further investigation. It is mentioned in the literature that the basic synthesis solution of MCM-41 ($pH\geq10$) may not allow the incorporation of metal cation dopants into the silica framework and may lead to precipitation of metal [50]. Main objectives of the present work were to obtain detailed comparative information for the activities of Ni and Cu metals in steam reforming of acetic acid, to have a better insight about the reaction paths over these catalytic materials, as well as to investigate the suitability of MCM-41 and Zr-MCM-41 as the support materials of the catalysts synthesized for this purpose.

2. Experimental

2.1.Catalyst Preparation

Mesoporous MCM-41 support was synthesized following a hydrothermal procedure similar to the route described by Arbag et al [45]. In this procedure, a solution containing dissolved surfactant (hexadecyltrimethylammonium bromide- CTMABr, Merck 99% pure) was continuously stirred at 28-30°C, until a clear solution was obtained. Sodium silicate (%27 SiO₂ + %8 Na₂O + %65 H₂O, Merck), which was used as the silica source, was added dropwise to the surfactant solution. Final pH of this solution was adjusted to 11 using sulfuric acid (4N, Merck). A gel was formed and it was transferred into a Teflon-lined stainless steel autoclave for hydrothermal synthesis for 96 h, at 120°C. The resulting solid product was filtered, washed several times until the pH of the wash liquid was set to a constant value and then dried for 24h. Calcination of the solid product was then performed in a tubular furnace, in a flow of dry air, at 750°C. In the case of synthesis of Zr incorporated MCM-41-like material, a similar one-pot hydrothermal route was followed. In this case, predetermined amount of zirconyl nitrate hydrate (Aldrich) was added into the surfactant solution, just after the sodium silicate addition step. The molar ratio of Zr/Si was selected as 0.25 basing on our earlier results, reported for zirconia incorporated SBA-15 type catalytic materials [46, 51]. Hydrothermal synthesis, drying and calcination steps were similar to the corresponding steps of MCM-41 synthesis route. This catalyst support material, containing a Zr/Si molar ratio of 0.25 is denoted as 25Zr-MCM-41.

MCM-41 or 25Zr-MCM-41 supported Ni and Cu containing catalysts were then prepared following a wet impregnation route. Nickel impregnated MCM-41 was prepared to obtain catalysts containing 1.0 wt %, 5.0 wt % and 10.0 wt % Ni and they were denoted as

1Ni@MCM-41, 5Ni@MCM-41 and 10Ni@MCM-41, respectively. In the case of copper impregnated material, Cu was impregnated to obtain a material containing 5 wt % Cu (5Cu@MCM-41). As for the 25Zr-MCM-41 supported materials are concerned, either 5 wt % Ni or 5 wt % Cu were impregnated and these materials were denoted as 5Ni@25Zr-MCM-41 and 5Cu@25Zr-MCM-41, respectively. Nickel nitrate hexahydrate (Ni(NO₃)₂.6H₂O, Merck) and copper nitrate hexahydrate (CuN₂O₆.3H₂O, Sigma-Aldrich) were used as the Ni and Cu precursors in the synthesis of these catalysts. After the evaporation step, these materials were dried in an oven and then calcined in a tubular furnace under the flow of dry air. Temperature of the calcination furnace was increased at a heating rate of 1°C/min, until 750°C was reached. Calcination was then continued for 6 hours at 750°C. These catalytic materials were then reduced at 750°C in a flow of hydrogen for 1 h, before the reaction tests.

2.2. Catalyst Characterization

Physical and structural properties of the synthesized catalysts were determined by performing X-ray diffraction (XRD), N₂ adsorption-desorption (BET), scanning electron microscopy (SEM) and inductively Coupled Plasma-Mass Spectrometer (ICP-MS). SEM and thermal analysis (TGA-DTA) of the spent catalysts were also performed to obtain information about coke deposition and possible structural changes of the catalysts during reaction.

XRD analysis of the fresh and spent catalysts were performed by using a Rigaku D/MAX 2200 instrument with a Cu K radiation source, at Middle East Technical University (METU) Central Laboratory. Characterization of the pore structures of the catalytic materials and BET surface area values were determined by means of the standard nitrogen adsorption/desorption technique, using a Quanta Chrome-Autosorb-6 sorptometer. SEM images of the fresh and the spent catalysts were obtained using a QUANTA 400F field emission scanning electron microscope, coupled with EDX. ICP-MS analysis of the materials was performed by a Perkin Elmer DRC II instrument. Thermogravimetric (TGA) and differential thermal analysis (DTA) of spent catalysts were made by means of Setaram Setsys-1750 TG-DTA System. These tests were performed in a stream of dry air by changing the temperature from 30°C to 900°C, at a heating rate of 10°C/min.

2.3. Catalytic Activity Tests

Catalytic performances of the synthesized catalytic materials were tested in the steam reforming reaction of acetic acid. These tests were performed in a quartz tubular flow reactor, having an inner diameter of 6 mm, at 750°C. Most of the activity tests lasted for three hours. Catalyst particles were packed into the center of the tubular reactor and supported from both ends by quartz wool. Particle size range of the catalyst was 1-2 mm and 0.1 g of fresh catalyst was used in each test. Acetic acid (AcOH) water mixture, with a pre-determined ratio, was injected to the reaction system using a syringe pump. Acetic acid/water mixture was evaporated within the evaporator of the reaction system at 140°C, where it was mixed with the carrier gas Argon. This mixture was then sent to the tubular flow reactor. Total flow rate of the reactor feed stream was adjusted to 82.5 ml/min (Space time = 0.072 g s/mL). Composition of the feed stream was adjusted as $(AcOH/H_2O/Ar)=(1.0/2.5/2.0 \text{ in molar ratio})$. Composition of the product stream leaving the reactor was analyzed using a gas chromatograph (GC, Agilent Model 6890N), which was connected on-line to the reactor exit stream. This gas chromatograph was equipped with a thermal conductivity detector and Porapak-S column. A condenser was placed between the tubular reactor outlet and gas chromatograph to collect the condensable components of the reactor exit stream. Analysis of this condensed phase indicated that it contained mainly water and small amount of unreacted acetic acid in some experiments.

Conversions of AcOH and product selectivity values were evaluated basing on the analysis of the product stream compositions and the results were checked by a carbon balance.

AcOH Conversion: $X_{AcOH} = [(AcOH_{in}-AcOH_{out})/AcOH_{in}]x100$

Selectivity of Hydrogen: $S_{H2} = [(Moles of H_2 \text{ produced})/(4xMoles of AcOH reacted})]x100$

Selectivities of CO, CO₂, CH₄:

 $S_i = [(Moles of compound i produced)/(2xMoles of AcOH reacted)]x100$

Moles of AcOH reacted= $(AcOH_{in}-AcOH_{out}) = (1/2)(CH_4 + CO_2 + CO)_{in product stream}$

3. RESULTS AND DISCUSSIONS

3.1. Characterization Results

Low angle XRD patterns of the synthesized silicate structured catalyst support clearly showed that the ordered pore structure of MCM-41 was formed (Fig. 1a). The main XRD peak observed at a 2 θ value of 2.40° (corresponding to d_{100}) and the three reflection peaks at 2 θ values 4.08°, 4.66° and 6.19° is a clear indication of MCM-41 structure. However, the low angle XRD pattern of zirconia incorporated MCM-41 (25Zr-MCM-41) was quite different, indicating that the ordered pore structure was not formed (Fig. 1a).

Nitrogen adsorption/desorption isotherm of MCM-41 support material also supported the formation of the ordered pore structure in the mesopore range (Fig. 2a). The shape of the isotherm (Type IV) supported the formation of an ordered mesoporous structure. On the other hand, N₂ adsorption/desorption behavior of zirconia incorporated MCM-41 did not show the characteristic hysteresis loop of MCM-41 type material having ordered pore structure. These results proved that, the zirconia incorporated silicate structured material (25Zr-MCM-41) did not contain an ordered pore structure but it was mesoporous.

XRD patterns and nitrogen adsorption/desorption isotherms of Ni impregnated MCM-41 type catalysts (Fig 1b and Fig 2b, respectively) showed that the ordered pore structure of MCM-41 was not significantly altered as a result of Ni impregnation. However, significant changes were observed both in the XRD patterns (Fig 1c) and N₂ adsorption/desorption isotherm (Fig. 2b) of the Cu impregnated materials. Ordered mesopore structure of MCM-41 was significantly deformed as a result of Cu impregnation. Sintering and strong interaction of copper with the support material during the calcination/reduction steps is considered as the main reasons of these structural changes. As it was also reported in the literature, copper was expected to sinter and form agglomerates at temperatures higher than of 350°C [52-55]. Pore-size distribution of 5Cu@MCM-41 was also found to be quite different than the pore-size distributions of MCM-41 and Ni impregnated MCM-41 materials (Fig. 3). Formation of a bimodal pore-size distribution in the Cu impregnated MCM-41 is also considered to be due to strong interaction of copper with SiO₂ via OH groups on the surface of the support. Formation of Cu-Si alloy was also reported in the literature at the calcination temperature of this material [56].

Some physical properties of the synthesized catalysts are given in Table 1. The surface area, average pore diameter and pore volume of MCM-41 decreased from 1213 m²/g to 761 m²/g, from 2.73 nm to 2.45 nm and from 1.15 cc/g to 0.64 cc/g, respectively, as a result of impregnation of 1% Ni. These results indicated that most of the Ni was penetrated into the

mesopores and deposited on the pore surfaces of this catalyst. This was also supported by the shift of pore-size distribution to smaller pores as a result of impregnation of Ni (Fig.3). It was quite surprising to observe that increase of Ni content of the catalyst from 1% to 5-10% did not cause further decrease in pore volume and pore diameter values of the synthesized materials. Even some increase was observed in the surface area of the impregnated MCM-41 as a result of increase of Ni content from 1% to 5-10%. These results indicated that some fraction of nickel was deposited on the external surface of MCM-41 for 5Ni@MCM-41 and 10Ni@MCM-41. XRD analysis results of the synthesized materials also supported these conclusions (Fig. 4). The nickel peaks observed in the XRD patterns of 1Ni@MCM-41 were extremely small. This result indicated that the crystal size of nickel was very small and nickel was very well dispersed within the pores of MCM-41. However, quite sharp Ni⁰ peaks were observed at 20 values of 44.62°, 51.92° and 76.54° in the XRD patterns of the reduced catalysts containing 5% and 10% nickel (5Ni@MCM-41 and 10Ni@MCM-41). Also, the absence of the peaks at 20 values of 37.3 °, 43.3 ° and 62.8° in these XRD patterns indicated that there were no NiO clusters detectable by XRD in the reduced materials. The crystal sizes of nickel, estimated from the XRD patterns using the Scherrer equation, were 15 nm and 22 nm for 5Ni@MCM-41 and 10Ni@MCM-41, respectively. These crystal sizes are larger than the average pore diameter of MCM-41, supporting that significant fraction of nickel was deposited on the external surface of the MCM-41 particles for these two catalytic materials. SEM-EDX mappings of Ni impregnated MCM-41 type catalysts also clearly indicated well dispersion of this metal within pore network (Fig. 5).

In the case of Cu impregnated MCM-41 (5Cu@MCM-41), decrease of surface area and the pore volume values were more significant than the case observed for 5Ni@MCM-41 (Table 1). Low angle XRD patterns (Fig 1c) and nitrogen adsorption isotherms of 5Cu@MCM-41 supported the conclusion that the ordered pore structure of MCM-41 was significantly deformed as a result of copper impregnation. As discussed above, sintering and of copper at temperatures over 350°C and its interaction with the silicate structured support are considered as the main reasons of this deformation. Wide angle XRD patterns of the 5Cu@MCM-41 showed typical peaks corresponding to metallic Cu clusters at 20 values of 43.38°, 50.51° and 74.16° (Fig. 4). Similar peaks were reported by Dong et al [56]. The crystal size of copper was estimated as 20 nm in this catalyst.

Surface area values of Ni and Cu impregnated 25Zr-MCM-41 type catalytic materials were also sufficiently high for catalytic purposes (Table 1). Their pore size distributions indicated the presence of pores mainly in the range of 5-200 nm. These materials were also

mesoporous, but did not contain ordered pore structures. ICP-MS analysis of these materials showed that zirconia was successfully incorporated into the silicate structure material.

As shown in Figure 4, the XRD patterns of Ni or Cu impregnated Zr-MCM-41 catalysts are consistent with the results of ICP-MS analysis, indicating the presence of zirconia phase. In the XRD patterns of these catalysts, the characteristic peaks of the tetragonal zirconia phase at around 30.12°, 34.52°, 50.6° and 59.69° were observed.

Sample	Procedure	Metal content in	Surface	Mean Pore	Pore
		Synthesis	Area,	Diameter,	Volume,
		Solution (wt%)	m²/g	nm	cc/g
MCM-41	Hydrothermal	-	1213	2.73	1.17
5Cu@MCM-41	Cu impregnated Hydrothermal	5% Cu	399		0.29
1Ni@MCM-41	Ni impregnated Hydrothermal	1% Ni	761	2.45	0.64
5Ni@MCM-41	Ni impregnated Hydrothermal	5% Ni	850	2.46	0.76
10Ni@MCM-41	Ni impregnated Hydrothermal	10% Ni	919	2.46	0.67
25Zr-MCM-41	One-pot hydrothermal	Y	350		0.87
5Ni@25Zr-MCM-41	Ni impregnated	5% Ni	88		0.48
5Cu@25Zr-MCM-41	Cu impregnated	5% Cu	110		0.45

Table 1. Physical properties of the synthesized catalysts





Figure 1. Low angle XRD patterns of (a) MCM-41, 25Zr-MCM-41, (b) 5Ni@MCM-41, (c) 5Cu@MCM-41





Figure 2. Nitrogen adsorption/desorption isotherms



Figure 3. Pore-size distributions of MCM-41, 1Ni@MCM-41 5Ni@MCM-41, 10Ni@MCM-41 and 5Cu@MCM-41.



Figure 4. XRD patterns of (a) reduced Ni based MCM-41, 25Zr-MCM-41, (b) reduced fresh and spent Cu based MCM-41, 25Zr-MCM-41, (c) spent 5Ni@MCM-41 and 5Ni@25Zr-MCM-41catalysts. (●Ni; *Cu; ■ZrO₂)



Si (green) Ni (blue) Figure 5. SEM image and Si, Ni EDX mappings of Ni impregnated MCM-41.

3.2.Activity Test Results

A series of catalytic activity tests were performed within a reaction period of 3 h at 750°C. The performances of the synthesized catalytic materials were evaluated in terms of AcOH conversion and selectivity values of H₂, CO₂, CO and CH₄. Before the activity tests, which were performed with the synthesized catalysts, reaction experiments were made without loading the catalysts into the quartz reactor, with the same feed composition and with the same feed flow rate of 82.5 ml/min, at 750°C. In these experiments, close to 60% initial acetic acid conversion values were obtained, due to thermal decarboxylation reaction. No hydrogen formation was observed in these tests. Formation of only CO₂ and CH₄, with close to equal mole fractions, was observed. These results indicated that the only reaction taking place in the absence of catalyst was decarboxylation reaction of AcOH.

$CH_3COOH \leftrightarrow CH_4 + CO_2$

Another set of initial experiments were also performed by packing the reactor with quartz particles instead of synthesized catalysts. These experiments were performed with the same feed composition and feed flow rate and at the same temperature of 750° C. The only products observed in these tests were also CH₄ and CO₂, supporting the conclusion that the only reaction that took place in the absence of a catalyst is decarboxylation of acetic acid. However, the results of these tests indicated lower conversion values of acetic acid (about 22 %) than the conversion obtained in an empty tubular reactor. This was simply because of lower mean residence time of reacting species within the fixed bed than the empty tubular reactor. Since, the inlet volumetric flow rates of the reactants in the experiments performed with the quartz filled and empty tubular reactors were the same, higher velocity and hence lower residence time of reactants is expected in the quartz filled system.

Acetic acid conversion values obtained with the MCM-41 supported catalysts are reported in Fig. 6. As shown in this figure, AcOH conversions obtained with pure MCM-41 and 5Cu@MCM-41 were highly unstable and much lower than the conversion values obtained with the Ni impregnated materials. In the presence of Cu impregnated catalyst, conversion of AcOH decreased from 80% to about 40% within a reaction period of three hours. In the case of pure MCM-41, conversion of AcOH decreased to a value of about 20%, which was about the same as in the case of the quartz filled reactor. As discussed above, this conversion value was lower than the conversion of AcOH observed in the absence of any packing in the reactor. This was simply because of longer residence time of species in the empty tubular reactor than the fixed bed reactors.

Highest activity was observed with the catalyst containing 5% Ni (5Ni@MCM-41). For this catalyst, complete conversion of AcOH was observed at initial reaction times. Some decrease of conversion observed at longer reaction times was considered to be mainly due to t deactivation of the catalyst as a result of coke formation. Further increase of Ni content of the catalyst from 5% to 10% did not cause further increase in activity. On the contrary, faster deactivation of the catalyst was observed with 10Ni@MCM-41, than 5Ni@MCM-41. This was considered to be due to larger crystal size of Ni in this catalyst. Catalytic performance of the material containing 1% Ni was not as good as the performance of 5Ni@MCM-41, indicating that amount of active sites for the steam reforming reaction were not sufficiently high within this material.



Figure 6. Variation of AcOH conversions over the MCM-41 supported catalysts at 750°C.

Product distributions obtained over the MCM-41 supported catalysts indicated that, hydrogen selectivity values were very low over MCM-41 and 5Cu@MCM-41, indicating that the catalytic performances of these materials were poor for the steam reforming reaction of acetic acid (Fig. 7). However, quite high and rather stable H₂ selectivity values were obtained over the 5Ni@MCM-41 and 10Ni@MCM-41. This result is due to high activity of Ni in steam reforming reactions by breaking the C-C, C-H and O-H bonds.



Figure 7. Hydrogen selectivity values over the MCM-41 supported catalytic materials.

Selectivity values of CO₂, CH₄ and CO reported in Fig.8 also supported the conclusion obtained from the hydrogen selectivity values reported in Fig.7. With 5Ni@MCM-41 and 10Ni@MCM-41, quite stable CO₂ and CO selectivity values of about 42% and 55% were obtained, respectively. Experimental selectivity values of H₂, CO and CO₂ were very close the equilibrium selectivities (71%, 56% and 43%, respectively), which were predicted from thermodynamic calculations. These catalysts showed very high activity for steam reforming reaction of AcOH. Methane selectivity was quite low (less than 5%) over these catalysts, indicating further reforming of any methane formed in this processes with H₂O or CO₂ (R.5 and R.6). A separate reaction test performed with a feed stream containing higher H₂O/AcOH molar ratio (30/1) showed that CH₄ was completely disappeared in the product stream. In that test, stable product distributions, composed of 66.7% H₂, 30.9% CO₂ and small amount of CO (2.9%), were observed.

Results reported in Fig.8b showed that, quite high methane formation was observed over 5Cu@MCM-41. This result supported the conclusion that copper based catalyst prepared in this

work was not active for the AcOH reforming reaction. Sintering and aggregation of copper species at temperatures over 350°C are expected to cause irreversible deactivation of copper based catalysts [52-55]. Nitrogen adsorption-desorption isotherm of 5Cu@MCM-41 catalyst supported this conclusion, indicating that Cu incorporation decreased the pore volume of MCM-41 material significantly. Although the XRD patterns of the Cu impregnated materials synthesized in the present study did not show the characteristic peaks of copper silicate, possible formation of a Cu-Si alloy and copper phyllosilicate were reported in the literature at the synthesis and reaction temperatures of the present study [52,53, 55].

Comparison of the AcOH conversion values of the Cu and Ni based catalysts supported on either MCM-41 or 25Zr-MCM-41 showed that the catalytic performances of the zirconia incorporated MCM-41 type catalysts were better. As shown in Fig.9, quite stable complete conversion of AcOH was observed over 5Ni@25Zr-MCM-41 during a reaction period of three hours. However, some decrease of AcOH conversion was observed with the 5Ni@MCM-41 catalyst, within the same reaction period. Results proved that Zr incorporation improved the stability of the MCM-41 supported Ni catalyst.

Comparison of hydrogen selectivity values obtained using Ni or Cu impregnated MCM-41 and 25Zr-MCM-41 catalysts also supported the conclusion that 5Ni@25Zr-MCM-41 gave the best performance, giving the highest H₂ selectivity and the most stable activity (Fig. 10). Product distributions obtained with 5Ni@25Zr-MCM-41 also supported this conclusion (Fig.11). Highly stable hydrogen (~60%), CO (~21%) and CO₂ (~19%) compositions were obtained over this catalyst. Absence of CH₄ in the product stream is another important superiority of this catalyst over the MCM-41 supported catalytic materials. The absence of CH₄ in the product stream was also reported by Vagia and Lemonidou over a Ni supported ceriazirconia catalyst at 750°C [57].

Comparison of the AcOH conversion values obtained with 5Cu@MCM-41 and 5Cu@25Zr-MCM-41 catalysts (Fig. 9) also supported the conclusion that the activity of the Zr incorporated MCM-41 type catalyst was higher than the activity of MCM-41 supported catalyst. However, the stability of the 5Cu@25Zr-MCM-41 was not good.



Figure 8. Product selectivities over MCM-41 supported catalysts with a feed stream composition of AcOH/H₂O/Ar=1.0/2.5/2.0: (a) CO₂; (b) CH₄; (c) CO



Figure 9. Comparison of AcOH conversions obtained with Ni and Cu based catalysts over MCM-41 and 25Zr-MCM-41 type catalytic materials. (AcOH/H₂O/Ar=1.0/2.5/2.0; T=750°C)



Figure 10. Comparison of hydrogen selectivity values of MCM-41 and 25Zr-MCM-41 supported Ni and Cu catalysts.



Figure 11. Product distributions over 5Ni@25Zr-MCM-41 catalyst

All of the catalytic activity tests reported above were performed for a reaction period of three hours, using 0.1 g catalyst. In order to observe catalyst deactivation at longer times, timeon stream tests extending to 12 hours were performed using 0.05 g 5Ni@25Zr-MCM-41. Due to decrease of catalyst amount from 0.1 g to 0.05 g, slight decrease of initial conversion of AcOH from 100% to 98% was observed in these tests. More importantly, decrease of conversion of AcOH to about 70% was observed after a reaction period of 12 hours. This was considered to be caused by deactivation of the catalyst due to coke formation at longer reaction times. However, product distributions were highly stable during the 12 hour tests.

After the 12 hour activity test of 5Ni@25Zr-MCM-41, spent catalyst was regenerated at 750°C, using air flow for 90 minutes and then using hydrogen flow for 60 minutes. Catalytic performance of the regenerated catalyst was tested again at 750°C, using 0.05 g catalyst. After the regeneration step, initial AcOH conversion reached to about 98%, which was about the same as it was observed with the fresh catalyst. Decrease of this conversion to about 60% was observed after a reaction period of four hours, which was again due to coke formation. However, the product selectivity values observed with the regenerated catalyst were highly stable within the reaction period of four hours (Fig. 12).



Figure 12. Product distributions observed with the regenerated 5Ni@25Zr-MCM-41 catalyst at 750°C.

3.3.Coke Formation and Characterization of Spent Catalysts

Thermogravimetric and differential thermal analysis (TG-DTA) and SEM tests were performed to obtain more information about coke formation and structural properties of spent catalysts. TGA–DTA was performed in a flow of dry air. Results of TGA-DTA of the spent

catalysts (5Ni@MCM-41, 5Cu@MCM-41 and 5Ni@25Zr-MCM-41) are shown in Figures 13 and 14. Significant weight loss was observed in the TGA of spent catalysts in the temperature range of 500–800°C. This weight loss is due to combustion of coke deposited on the catalyst. Results showed more coke formation over Ni impregnated MCM-41 than Cu impregnated MCM-41. Zr incorporation decreased the crystal size of Ni and Cu in the catalyst (Table 2). In parallel to this observation, coke deposition over Ni based catalyst was also decreased as a result of Zr incorporation into the MCM-41 like support material.

Table 2. Crystal sizes of the Ni and Cu in MCM-41 and Zr-MCM-41 catalysts before activity tests

Catalysts	Crystal Size, nm
5Ni@MCM-41	15.5
5Ni@25Zr-MCM-41	11.4
5Cu@MCM-41	20.0
5Cu@25Zr-MCM-41	15.0



Figure 13. TG analysis of spent 5Ni@MCM-41, 5Cu@MCM-41 and 5Ni@25Zr-MCM-41 catalysts after 3 h of reaction time.

DTA analyses of the spent 5Ni@MCM-41, 5Cu@MCM-41 and 5Ni@25Zr-MCM-41 are reported in Figure 14. As shown in this figure, coke removal due to combustion takes place in the temperature range of 450-800°C for MCM-41 supported Ni and Cu catalysts. In fact, two distinct peaks were observed in the temperature ranges of 450-700°C and 750-800°C in the DTA of spent 5Ni@MCM-41. Amorphous and filamentous carbon was expected to be

combusted at lower temperatures [51]. On the other hand, graphitic carbon was expected to be burned at temperatures higher than 750°C. This result showed that both filamentous and graphitic carbons were formed over the MCM-41 supported catalysts. However, in the case of 25Zr-MCM-41 supported catalyst, coke removal was achieved in the temperature range of 450-670°C, indicating that graphitic carbon was not formed over this material. Sharp XRD peak observed at $2\theta=26^{\circ}$ in the XRD pattern of spent 5Ni@MCM-41 (Fig.4) supported the formation of graphitic carbon over this material.



Figure 14. DT analysis of spent 5Ni@MCM-41, 5Cu@MCM-41, and 5Ni@25Zr-MCM-41 catalysts after 3 h of reaction time.

Comparison of SEM images of fresh and spent 5Ni@MCM-41 catalyst also showed the formation of carbon filaments on the surface of used 5Ni@MCM-41 after the 3 h of reaction test (Figure 15). Analysis of the dimensions of these carbon filaments showed that their diameters were in the range of 11–26 nm.





b)

Figure 15. SEM images of a) 5Ni@MCM-41 b) used 5Ni@MCM-41

4. CONCLUSIONS

A new mesoporous catalyst support material was synthesized by the incorporation of Zr into the MCM-41 structure through a one-pot procedure. Ni impregnated 25Zr-MCM-41 was shown to give highly stable performance in steam reforming of acetic acid. Experimental results obtained for steam reforming acetic acid at 750°C over Ni impregnated MCM-41 and the

zirconia incorporated MCM-41-like mesoporous material gave very high AcOH conversions and hydrogen yields. Product compositions obtained with these catalysts were shown to be close to the equilibrium compositions predicted from thermodynamic analysis of the system. It was concluded that incorporation of zirconia into the structure of MCM-41 through a one-pot procedure enhanced the activity, as well as the stability of the Ni impregnated catalysts for steam reforming of acetic acid. Minimization of CH₄ in the product stream was an added advantage of this catalyst. Amount of impregnated Ni was also shown to be quite important in terms of activity and stability of the synthesized catalytic materials. Optimum Ni content of the catalysts was found as 5%. Catalytic performance of the material containing 10% Ni was not as good as the catalyst containing 5% Ni, just because of the formation of larger Ni crystals. Another advantage of zirconia incorporated MCM-41 support over MCM-41 is that graphitic carbon was not formed over 5Ni@25Zr-MCM-41. Coke formed over this material was easily removed from the catalyst surface by combustion at temperatures lower than 670°C. It was concluded that 5Ni@25Zr-MCM-41 was a highly promising catalyst for hydrogen production through steam reforming of acetic acid.

Catalytic performances of Cu impregnated silicate structured mesoporous materials MCM-41 and 25Zr-MCM-41 were poor in terms of steam reforming reactions. Large fractions of CH₄ and CO₂ present in the product streams indicated the occurrence of decarboxylation reaction of AcOH rather than the reforming reactions in the presence of Cu impregnated catalysts. Hydrogen yield values were also quite low over the Cu impregnated materials. Sintering of copper species and strong interaction of Cu with the silicate structured support caused catalyst deactivation, as well as deformations in the ordered pore structure of the support materials.

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