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Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Synthesis, textural and catalytic properties of nanosized Fe₂O₃/MgO system



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ARTICLE INFO

Article history: Received 18 February 2013 Received in revised form 11 May 2013 Accepted 16 June 2013 Available online 24 June 2013

Keywords: A. Microporous materials A. Nanostructures C. X-ray diffraction D. Catalytic properties D. Electronic paramagnetic resonance (EPR)

ABSTRACT

FeMgO system was prepared by three different methods. The samples were nominated as FeMgO_{IM}, FeMgO_{Co} and FeMgO_{HY} due to preparation by impregnation, co-precipitation and hydrothermal, respectively. The catalysts were characterized by TGA, XRD, FTIR, EPR, S_{BET} and TEM techniques. The catalytic properties of these samples were investigated by using H₂O₂ decomposition at (25–35 °C) and partial oxidation of methanol at (300–400 °C). FeMgO_{HY} sample showed the highest catalytic activity toward H₂O₂ decomposition. FeMgO_{Co} sample showed the highest catalytic activity toward H₂O₂ decomposition. The results showed the sensitivity of H₂O₂ decomposition reaction to the surface concentration of active species. While partial oxidation of methanol is sensitive to surface texture, solids interaction between active phase and support. All catalysts are highly selective to formaldehyde at reaction temperature 300 °C. FeMgO_{Co} and FeMgO_{IM} catalysts showed high catalytic activity and stability toward partial oxidation of methanol of methanol with reusing.

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1. Introduction

Because of their unique properties, intensive research efforts have been devoted to nanosized metal oxides preparation [1]. The composition, preparation procedure and pretreatment conditions strongly affect on the catalytic properties of nanosized materials [2,3]. Controlled particle size and shape metal oxides exhibit densely populated unsaturated surface coordination sites. These sites are responsible for improving the catalytic performance [4]. Various methods have been proposed for metal oxides preparation, such as sol-gel [5], impregnation [6], co-precipitation [7] and hydrothermal [8]. It has been reported that wet impregnation method allows obtaining supported catalysts and co-precipitation yields "bulk" mixtures [9]. While hydrothermal method yields highly homogeneous crystalline product directly at a relatively lower reaction temperature. It favors a decrease in agglomeration between particles, phase homogeneity, uniform composition, high product purity and controlled particle morphology [10].

Nanosized iron oxide showed a great activity in the oxidation reactions instead of noble metals [11]. Supporting iron oxide resulted modifications of its textural, structural, and catalytic properties [12]. MgO is a ceramic oxide used as a catalyst and support for many materials having biomedical applications [13]. Fe₂O₃/MgO-based catalysts have been used for many redox reactions as H_2O_2 decompositions [4]. H_2O_2 is used as a green fuel/propellant instead of carcinogenic hydrazine in spaceflight under certain conditions [14], and instead of liquid oxygen as an oxidizer in fuel cells [15]. Decomposition of H_2O_2 yielding oxygen over metal oxides and their mixtures has been investigated previously [16]. Also, supported iron oxide was used as a catalyst for methanol partial oxidation to give formate species [17]. Formaldehyde is an important intermediate in many chemical industries, such as production of adhesives, molding compounds and coating resins [18]. It has been reported that formaldehyde is formed by a combination of oxidative and non-oxidative dehydrogenation of methanol [19].

Production of formaldehyde from methanol and air is done with either methanol-rich or methanol-lean feed using the silver and oxide process, respectively [19]. Due to methanol price duplication, oxide process has been favored the last years [19,20,21]. Many catalytic systems were investigated in methanol oxidation to formaldehyde such as FeVO₄ [22], α -Al₂O₃-, SiO₂- and TiO₂supported Fe–V–O [23].

In this paper, we aimed to investigate the effect of preparation methods of the Fe₂O₃/MgO system on its physicochemical, surface and the catalytic properties toward two redox reactions are catalytic decomposition of hydrogen peroxide at 25–35 °C and conversion of methanol at 300–400 °C using the flow system and. The techniques employed were TG/DTG, XRD, EPR, TEM and nitrogen adsorption at–196 °C.

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2. Experimental

2.1. Preparation of FeMgO system

Three Fe_2O_3/MgO catalysts having the formula $0.045Fe_2O_3/MgO$ were prepared by three different methods namely: wet impregnation (IM), co-precipitation (Co) and hydrothermal (HY) methods. Fe_2O_3 mass content (wt %) in these samples was fixed at 15.2%. All the employed chemicals were of analytical grade and supplied by BDH Company (UK).

2.1.1. Wet impregnation method (IM)

The sample was prepared by impregnation a known amount of magnesium hydroxide, which was prepared previously [4], with a known amount of iron nitrate dissolved in the least amount of bidistilled water necessary to make a paste. The resulting paste was dried at 110 °C and then calcined at 500 °C for 4 h. This sample was nominated as FeMgO_{IM}.

2.1.2. Co-precipitation method (Co)

The sample was prepared by co-precipitation iron and magnesium hydroxides at room temperature using corresponding amounts of iron and magnesium nitrates and 0.2 M NH₄OH at pH 8. The precipitate was filtered and washed with bi-distilled water. The obtained hydroxide was dried at 110 °C and then calcined in air at 500 °C for 4 h. This sample was nominated as FeMgO_{Co}.

2.1.3. Hydrothermal method (HY)

The coprecipitated iron-magnesium hydroxides sample at 25 °C, was suspended in 30 ml bi-distilled water. The obtained suspension was placed into a 45 ml Teflon-lined autoclave and then heated at 200 °C at vapor pressure15 atm for 1 h. Then autoclave was quenched to room temperature and the resulting colloidal iron/magnesium hydroxide was heated at 50 °C for several hours to remove water [24]. The obtained solid was calcined in air at 500 °C for 4 h. This sample was nominated as FeMgO_{HY}.

2.2. Techniques

Thermogravimetric analysis (TGA) of the catalysts was performed using a Shimadzu TGA-50H thermogravimetric analyzer (Japan); the rate of heating was kept at $10 \,^{\circ}\text{C} \text{min}^{-1}$ and the flow rate of nitrogen was 30 ml/min.

X-ray diffractograms (XRD) were obtained using Brucker Axs D8 Advance X-ray diffractometer (Germany), using Cu K α_1 irradiation (λ = 0.15404 Å) at a scan rate of 2° in 2 θ /min. The accelerating voltage and applied current were 40 kV and 40 mA, respectively. The crystallite sizes of the investigated phases were calculated using Scherrer equation [25], Fourier transform infrared (FTIR) spectroscopy of different samples were recorded on a Jasco IR 4100 spectrometer (Japan) using KBr pellets in the range of 4000–400 cm⁻¹ region.

The EPR investigations were performed at laboratory temperature using a Brucker spectrometer (Germany) at a frequency of 9.7 GHz (X band) for cavity operating. The catalysts were activated at laboratory temperature under vacuum by a short evacuation.

The surface characteristics of the prepared catalysts were determined from nitrogen adsorption isotherms measured at-196 °C using a Quantachrome NOVA 2000 automated gas-sorption apparatus model 7.11 (USA). The surface characteristics include specific surface areas (S_{BET}), total pore volume (V_p) and average pore radius (\hat{r}). All catalysts were degassed at 200 °C for 2 h under a reduced pressure of 1.3 mPa before taking such measurements.

Morphology of the samples was investigated using transmission electron microscope (TEM) (JEM-2100CX (JEOL).

The catalytic activities of the various solid catalyst samples were determined by using methanol conversion reaction at different temperatures varying between 300 and 400 °C. The catalytic reaction was conducted in a flow reactor under atmospheric pressure. Thus, a 50 mg catalyst sample was held between two glass wool plugs in a Pyrex glass reactor tube 20 cm long and 1 cm internal diameter packed with quartz fragments 2-3 mm length. The temperature of the catalyst bed was regulated and controlled within ± 1 °C. Argon gas was used as the diluent and the methanol vapor was introduced into the reactor through an evaporator/saturator containing the liquid reactant at constant temperature 35 °C. The flow rate of the argon was maintained at 25 ml/min. Before carrying out catalytic activity measurements each catalyst sample was activated by heating at 300 °C in a current of argon for 1 h then cooled to the catalytic reaction temperature. The injection time of the sample products and the unreacted methanol was fixed after 15 min, and many injections were carried out to give constant conversion. The reaction products in the gaseous phase were analyzed chromatographically using Perkin-Elmer Auto System XL Gas Chromatograph fitted with a flame ionization detector. The column used was stainless steel chromatographic columns, 4 m length, packed with 10% squalane supported on chromosorb. The reaction products were analyzed at a column temperature of 40 °C in all conversion runs. Detector temperature was kept at 250 °C.

The catalytic decomposition of H_2O_2 in presence of the prepared catalysts was also determined. 100 mg of a given catalyst sample was taken and 0.5 ml of H_2O_2 of known concentration diluted to 20 ml with distilled water was used at reaction temperature 25–35 °C. The reaction kinetics was monitored by measuring the volume of O_2 liberated at different time intervals until no further oxygen was liberated.

3. Results and discussions

3.1. Thermogravimetric analysis of the uncalcined FeMgO samples

Thermogravimetric analysis (TGA) of uncalcined FeMgO_{IM}, FeMgO_{Co} and FeMgO_{HY} samples were determined and the data are listed in Table 1. The TG curves of the investigated samples (not given here), consist of three stages. The first step represents the loss of surface-adsorbed water and some of crystallization water from iron nitrate. The second step is indicative to the complete decomposition of iron nitrate to Fe₂O₃ along with decomposition most of the magnesium hydroxide. The final step indicates the

Table 1

Effect of changing the preparation method on the thermal behavior of uncalcined of Fe_2O_3/MgO samples.

Sample	$T_1(^{\circ}C)$ (wt. loss%)	<i>T</i> ₂ (°C) (wt. loss %)	<i>T</i> ₃ (°C) (wt. loss %)	Total weight loss %		
				Calculated	Found	
FeMgO _{IM}	$Rt \rightarrow 156$ (8.6)	$156 \! ightarrow \! 422 \; (35.5)$	$422 { o} 739~(4.5)$	54.1	48.6	
FeMgO _{Co}	$Rt \rightarrow 193$ (10.2)	$193 \rightarrow 400 \ (20.1)$	$400 { o} 764~(9.7)$	40.9	40.0	
FeMgO _{HY}	$Rt {\rightarrow} 193~(11.4)$	$193 \to 356 (16.3)$	$356 \mathop{\rightarrow} 707\ (10.4)$	38.1	39.4	

Rt: room temperature.



Fig. 1. XRD pattern of different prepared FeMgO catalysts calcined at 500 °C. Lines (1) refer to MgO phase.

complete dehydroxylation of MgO and/or the removal of the residual OH groups bonded to the MgO lattice [4,26]. The difference in weight loss values of the investigated samples can be assigned to the incomplete desorption of the residual $\bar{O}H$ groups bonded to the MgO lattice in this temperature range [26]. The observed lower weight loss for uncalcined FeMgO_{Co} and FeMgO_{HY} samples may be due to formation spherical and nanorod particles. The observed higher weight loss for uncalcined FeMgO_{IM} sample may be due to formation microporous structure [27].

3.2. X-ray diffractograms of the prepared catalysts

X-ray diffraction technique was used to characterize FeMgO_{IM}, FeMgO_{Co} and FeMgO_{HY} catalysts calcined at 500 °C. The phase structure and the crystallite sizes of the investigated phases in these solids were investigated as shown in Fig. 1 and Table 2. The results showed that: (i) the diffractograms consist of MgO phase (periclase) (JCPDS 4-829). MgO phase appears with moderate degree of ordering in case of FeMgOIM sample, and with very low degree of crystallinity in case of FeMgO_{Co} and FeMgO_{HY} nanoparticles. The absence of Fe₂O₃ phase might indicate its presence in finely divided state beside its small amount to be detected by X-ray diffractometer [28]. So, magnesium oxide acts as a convenient support to hematite. The crystallite size of the detected MgO phase is \leq 21.7 nm. The crystallite size values of MgO phase present in the FeMgO_{Co} and FeMgO_{HY} catalysts were smaller than that found in FeMgO_{IM} sample. The value of calculated lattice constant of MgO phase was dependent on the preparation technique. It is observed that the lattice parameter of MgO in FeMgO_{HY} sample has the smallest value. This result could be explained on the light of the small particle size of MgO phase in FeMgO_{HY} sample [29].

3.3. FTIR spectra of the prepared catalysts

The FTIR spectra of the prepared catalysts were investigated as shown in Fig. 2. According to this figure there is a broad band at

Table 2

Intensity count, crystallite size and lattice parameter constant of MgO phase in the investigated samples calcined at 500 $^\circ \rm C.$

Sample	MgO		a-const [MgO] (Å) ^a
	Intensity count (a.u.)	Crystallite size (nm)	
FeMgO _{IM}	30.8	21.7	4.215
FeMgO _{Co}	7.4	9.1	4.212
FeMgO _{HY}	9.9	9.8	4.206

^a The standard a value of MgO is 4.213 Å.



Fig. 2. FTIR spectra of the catalysts: (a) $FeMgO_{IM},$ (b) $FeMgO_{Co}$ and (c) $FeMgO_{HY}$ calcined at 500 $^\circ C.$

3600–3200 cm⁻¹ due to adsorbed water molecules and O–H stretching of surface hydroxyls disturbed by the hydrogen bonds [30–32]. The observed broadening in this band in case of FeMgO_{HY} spectra (Fig. 2c) confirms a high degree of hydrogen bonding of water molecules among themselves and with the surface of MgO crystallites [33]. It is observed also presence band at 1640–1610 cm⁻¹ is due to O–H bending [12]. The band at 1100 cm⁻¹ is belonging to M–OH [31]. A broad band at 1460–1400 cm⁻¹ corresponds to the Mg–O stretching as well as the Mg–O–Mg deformation [32].

3.4. EPR of the prepared catalysts

The EPR spectra of the prepared catalysts calcined at 500 °C were investigated as shown in Fig. 3. Inspection of this figure there is a very broad ESR signal at $g \approx 2$ with very low, moderate and extremely high intensity for FeMgO_{IM}, FeMgO_{HY} and FeMgO_{Co} catalysts, respectively. This EPR signal could be due to Fe–O–Fe species with ferri-, ferro-, and/or antiferromagnetic behavior [34]. It can originate from various iron oxide species such as γ -Fe₂O₃ or Fe₃O₄ (both ferrimagnetic), or α -Fe₂O₃ (antiferromagnetic) [35]. It can be related to superoxide ions (O^{2–}) associated with Fe ions [36], or hydrated iron species [37]. The observed broadening of EPR signal at $g \approx 2$ could be due to partial reduction of a very small amount of Fe³⁺ to EPR-silent Fe²⁺ (or Fe⁰) species as shown in FeMgO_{HY} spectrum [38]. The observed increase in signal intensity



Fig. 3. Ambient temperature EPR spectra of different prepared FeMgO catalysts calcined at 500 $^\circ\text{C}.$



Fig. 4. Nitrogen adsorption/desorption isotherms (a) and V_L -t plots (b) of different prepared FeMgO catalysts calcined at 500 °C.

in case of FeMgO_{Co} and FeMgO_{HY} nanoparticles could be due to presence of super paramagnetic iron oxide nanoparticles [39]. The observed changes in the thermal, crystallographic, and spectral properties of FeMgO system can affect both its surface and catalytic properties.

3.5. Surface characteristics of FeMgO catalysts

The nitrogen adsorption/desorption isotherms of FeMgO nanoparticles were carried out as shown in Fig. 4a. These isotherms could be classified as type II of Brunauer's classification. Table 3 includes the surface characteristics of FeMgO nanoparticles. The specific surface areas (S_{BET}) were calculated by the BET method [40]. The total pore volumes, V_p were taken at $P/P^0 = 0.95$. The average pore radius (\hat{r}) was estimated from the relationship: $\hat{r} = 10^4 (2V_p/S_{BET})$. S_t and S_s surface areas were calculated by t-plot and α_s methods [41,42], respectively (as shown in Fig. 4b). α_s method is used also to calculate external and internal surface areas (S_{ext} and $T_{able} 3$: (i) S_{BET} and average pore radius (\hat{r}) of nano-sized FeMgO catalysts follow this order: FeMgO-HY < FeMgO_{IM} < FeMgO_{Co}. (ii) FeMgO_{IM} sample is a microporous material and its internal surface area is higher than the external

surface area. (iii) FeMgO_{Co} sample consists of meso- and micropores mixture while FeMgO_{HY} sample is mesoporous material. (iv) The values of S_{BET} , S_t and S_s are close to each other which justify the correct choice of standard *t*-curves used in the analysis. According to the obtained results, presence a mixture of meso- and micropores in FeMgO_{Co} sample could reduce transport limitations in catalysis, resulting in higher activities and better controlled selectivities [43].

3.6. TEM of the prepared catalysts

To investigate the effect of preparation method on the FeMgO nanoparticles morphology, TEM images were measured as shown in Fig. 5. This figure showed that: (i) TEM of FeMgO_{IM} solid contain aggregates of uniform trigonal shapes from MgO nanoparticles with average diameter 25 nm. (ii) TEM of FeMgO_{Co} sample contains uniform spherical nanoparticles with average diameter 7.9 nm. (iii) TEM of FeMgO_{HY} sample contains some nano-rods and uniform spherical nanoparticles of MgO. The average diameter of the spherical nanoparticles is 3 nm and the average diameters and lengths of the nano-rods are 9.1 and 43.5 nm, respectively. The average particle size calculated from the TEM micrographs is consistent with the average crystallite size obtained from XRD measurement. (iv) There are very small darker spots highly dispersed in the hydroxide or oxide layer. These spots correspond to very small iron oxide particles completely dispersed [44]. The presence relatively large sized uniform trigonal crystals in FeMgO_{IM} and FeMgO_{Co} samples could be due to rapid growing of Mg(OH)₂ precursor during its preparation by precipitation. In addition, calcination of this material affords MgO having correspondingly large particle size [45,46]. So, FeMgO_{IM} and FeMgO_{CO} samples calcined at 500 °C contain randomly distributed and highly aggregated nanoparticles, these aggregated nanoparticles exist in cluster format. These results confirm that the hydrothermal treatment play an important role in rod growing [47,48].

3.7. Catalytic activities of FeMgO catalysts

3.7.1. Catalytic decomposition of H_2O_2

The catalytic decomposition of H_2O_2 was studied at 25–35 °C over FeMgO_{IM}, FeMgO_{Co} and FeMgO_{HY} catalysts as shown in Fig. 6. This figure shows the first-order plots, its slopes allowed a ready determination of the reaction rate constant (k) at 30 °C. Inspection of Fig. 6 the catalytic activity of the investigated samples expressed as reaction rate constant k (min⁻¹) followed this order: FeMgO_{HY} > FeMgO_{Co} > FeMgO_{IM}. In other words, the solid prepared by hydrothermal method showed the biggest catalytic activity. To eliminate the role played by surface area, the values of reaction rate constant per unit surface area k^- (min⁻¹ m⁻²) at 30 °C were calculated to as shown in Fig. 7. Due to this figure, there is a big increase in the catalytic activity of FeMgO_{HY} in spite of its small surface area with comparison to FeMgO_{IM} and FeMgO_{Co} catalysts.

The obtained results could be explained on the light of the following: (i) The observed catalytic activity of FeMgO system toward decomposition of H_2O_2 refers to presence well-dispersed Fe₂O₃ particles in nanosize MgO support as shown in XRD and TEM sections. (ii) The observed higher catalytic activity of FeMgO_{HY} toward this reaction could be due to presence Fe²⁺ and Fe³⁺ species

Table 3

The	specific	surface	areas an	l pore	characteristics	of the	e FeMgO	samples	calcined	at 500 °C.	
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Samples	$S_{\text{BET}}(m^2/g)$	$S_t (m^2/g)$	$S_{\rm s} ({\rm m^2/g})$	$S_{\text{ext.}}$ (m ² /g)	$S_{\text{inter.}}(m^2/g)$	$V_{\rm p}~({\rm ml/g})$	ŕ (Å)
FeMgOIM	95.2	94.6	93.3	42.2	51.1	0.1497	31.5
FeMgOCo	99.1	100.5	100.7	-	-	0.2722	54.9
FeMgOHy	43.9	44.6	45.3	-	-	0.1469	66.8



Fig. 5. TEM images of (a) FeMgO_{IM}, (b) FeMgO_{Co} and (c) FeMgO_{HY} nanoparticles calcined at 500 °C.

[38] as shown in EPR section. Presence of Fe^{2+} ions increases the rate of the investigated catalytic reaction. It seems that catalytic decomposition of H_2O_2 is not much sensitive to the catalyst surface area enhancement while it is sensitive to presence transition metal ions with different oxidation states. (ii) Also, presence nano-rods in the morphology of FeMgO_{HY} sample as shown in the TEM of this sample could play an important role in enhancement of its catalytic activity toward this redox reaction.

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(iii) The catalytic activity of $FeMgO_{Co}$ was higher than that of $FeMgO_{IM}$ sample; this could be due to presence of various types of surface active oxygen species in $FeMgO_{Co}$ sample more than that

present in FeMgO_{IM} sample [49]. It has been reported that the reducible transition metal oxides such as Fe₂O₃ exhibit a significantly enhanced activity for oxidation reaction, which was attributed to their ability to provide reactive oxygen [50]. So, more oxygen vacancies may facilitate the adsorption of H₂O₂ and result in increasing the catalytic activity [51]. (iv) The possible dishomogeneity of iron cations distribution [52] on the surface may be responsible for the observed decrease in the catalytic activity of FeMgO_{IM} sample.

3.7.2. Partial catalytic oxidation of methanol

The catalytic conversion of methanol, at reaction temperature varied between 300 and 400 °C was carried out over fresh and reused FeMgO catalysts calcined at 500 °C. The catalytic activity



Fig. 6. First-order plots of H_2O_2 decomposition conducted at 30 $^\circ C$ over different prepared FeMgO catalysts calcined at 500 $^\circ C.$



Fig. 7. Variation of (k^-) toward H₂O₂ decomposition conducted at 30 °C over FeMgO catalysts calcined at 500 °C as a function of preparation method.

was expressed as a change in the total percentage conversion as shown in Fig. 8 and Table 4. The values of catalytic selectivities toward various products of methanol conversion in the gas phase were calculated and added in Table 4. The detected products of methanol conversion in presence FeMgO system were formaldehyde (FM), dimethyl ether (DME) and traces of methyl formate (MF). Inspection of Table 4 and Fig. 8: (i) the catalytic activity increased with increasing the reaction temperature from 300 to 400 °C. (ii) FeMgO_{Co} exhibited catalytic activity higher than that of FeMgO_{IM} and FeMgO_{HY} catalysts. (iii) All catalysts were highly selective to formaldehyde 100% at 300 °C; this selectivity was slightly decreased with increasing the reaction temperature especially in case of FeMgO_{CO} and FeMgO_{IM} catalysts. (iv) FeMgO_{HY} catalyst exhibited small selectivity toward DME in expense of formaldehyde selectivity at 350 °C. (v) Very small amounts of methyl formate and DME were detected at 400 °C. (vi) The total conversion decreased by reusing the catalysts (FeMgO_{Co} and FeMgO_{IM}) toward partial oxidation of methanol two times. The activity retained of these samples at 400 °C after reusing for two times was about 52%. (vii) The recycled FeMgO_{Co} and FeMgO_{IM} samples showed high stability toward formaldehyde selectivity and some fluctuation toward DME or methyl formate selectivity.

The obtained results can be explained as the following: (i) the catalytic activity of FeMgO catalyst toward partial oxidation of methanol to formaldehyde depends on presence nano-iron oxide [53,54] supported on magnesia. Presence these active species been inferred from the observed decrease in the degree of ordering and crystallite size of MgO as a support (cf. Table 2). (ii) The role of surface area is important in the interpretation the high catalytic activity of FeMgO_{Co} and FeMgO_{IM} with comparison to FeMgO_{HY} catalyst calcined at 500 °C (cf. Table 3). (iii) The most active one was FeMgO_{Co} catalyst. This activity is due to consistence meso and micro structure as shown in surface section. So, combination of smaller and larger mesopores could reduce transport limitations in catalysis, resulting in higher activities and better controlled selectivities [43]. (v) The observed low activity of FeMgO_{HY} calcined at 500 °C could be attributed to its smaller surface area as shown in Table 3 or, possible smaller number of active surface sites [56,57]. It has been reported by one of the authors that the surface concentration of iron species measured by EDX technique [58] was higher in case of the $FeMgO_{Co}$ and $FeMgO_{HY}$ samples with comparison to $FeMgO_{IM}$ sample calcined at 500 $^\circ\text{C}.$ So, in spite of this result the surface area parameter plays a dominant effect in conversion of methanol, where the surface area of FeMgO_{HY} was half the value of other two samples. Other item one cannot neglect was the ferrite formation, where FeMgO_{HY} sample was the most sample capable to form ferrite even at 500 °C [58]. It has been reported that Fe³⁺ has higher electronegativity as compared to Mg²⁺, and, formation of solid solutions having general composition



Fig. 8. Total conversion of methanol over (a) various catalysts as function of reaction temperature (b) $FeMgO_{Co}$ and $FeMgO_{HY}$ samples as a function of reusing times.

 $Mg_{1-x}Fe_xO_{1+0.5x}$ with medium-strength basic sites is reported [59]. So, the observed decrease in the catalytic activity and selectivity of FeMgO_{HY} calcined at 500 °C could be due to ferrite formation. (iv) Formaldehyde is produced according to dehydrogenation mechanism and the active sites are nanosized Fe³⁺ ions and mediumstrength basic active sites [Mg(M)–O] with high density [55]. The observed high selectivity of the FeMgO catalyst for formaldehyde production stresses on the role of magnesium ferrite in partial oxidation to formaldehyde, and supports the idea of disappearance Fe₂O₃ phase. Fe₂O₃ is known as an active catalyst to total oxidation of methanol [60]. (vi) The observed decrease in the formaldehyde selectivity in case of FeMgO_{HY} sample could be due to such higher degree of surface reduction during dehydrogenation process yielding Fe²⁺. This surface reduction would occur during

Table 4

Total conversion (T.C.) and selectivities to formaldehyde S_F, methyl formate S_{MF} and dimethyl ether S_{DME} over various prepared catalysts calcined at 500 °C.

Reaction temp. ($^{\circ}C$)	T.C. and selectivity (%)	Catalyst						
		FeMgO _{IM}	Recycle1	Recycle2	FeMgO _{Co}	Recycle1	Recycle2	FeMgO _{HY}
300	T.C.	0.44	0.25	0.17	0.60	0.43	0.18	0.16
	S _F	100	100	100	100	100	100	100
350	T.C.	4.0	3.9	2.0	7.3	6.5	3.8	3.0
	S _F	98.5	98.7	98	98.9	99.2	97.1	88.5
	S _{MF}	0.75	1.3	1.5	0	0	0	0
	S _{DME}	0.75	0	0.5	1.1	0.8	2.9	11.5
400	T.C.	29.6	27.0	15.5	27.1	23.6	12.6	22.2
	S _F	96.2	98	98.3	97.9	99.5	97.9	97.4
	S _{MF}	0.8	0.8	0.8	1.4 ^a	0	0.9	0.6
	S _{DME}	3.0 ^a	1.2 ^a	0.9 ^a	0.7	0.5	1.2	2.0

^a Others beside DME or MF.

calcination too [61]. It has been reported that the surface of coprecipitated sample has lower reducibility than other samples [61]. The observed increase in the EPR signal intensity for FeMgO_{Co} sample showed the high concentration of free iron species (not reduced) in the course of preparation and calcination while the lower intensity support the idea of lowering concentration of Fe³⁺ and possible formation Fe^{2+} species in $FeMgO_{HY}$ catalyst through preparation and calcination step. (vii) The observed selectivity of FeMgO_{HV} to DME could be due to formation nano-rods. It has been reported that Fe³⁺ possess significant acid properties because it occupies low-coordinated crystallographic positions and the coordination-non-saturated atom capable of creation more Lewis acid sites on the surface of samples [57]. But the possible decrease in surface concentration of Fe³⁺ (to give Fe²⁺) as shown in EPR and redox reaction of H₂O₂ may decrease the external surface Lewis acidity. It has been reported that the selectivity to DME was enhanced as the ZSM-5 crystal size of samples were reduced and it depends on the acid site distribution, and if there is less or even no acid site on the external surface, all of methanol could be converted to DME. It was also found that uniform ZSM-5 nanocrystals are the most selective catalyst to DME production [62]. According to these reported results one can explain the observed selectivity for FeMgO_{HY} sample toward DME due to presence some observed nano-rods with possible low concentration of surface acidity. (viii) Absence DME in case of FeMgO_{Co} and FeMgO_{IM} samples with comparison to FeMgO_{HY} is due to the role of dilution effect of iron oxide species by MgO support (due to increasing surface area and degree of dispersion as shown in XRD section). Where, it was profound on the dimethyl ether formation suggesting that the iron oxide surface atoms must be closely situated to promote the adsorption of two neighboring methanol groups as initially methoxy groups that subsequently combine to give dimethyl ether.

4. Conclusions

In conclusion, the physicochemical and catalytic properties of FeMgO system depend mainly on the preparation method, i.e. impregnation (IM), coprecipitation (Co) and hydrothermal (HY). The catalytic activity of the FeMgO system toward redox reaction as H₂O₂ decomposition is mainly determined by surface concentration of active species and presence transition metal ions with different oxidation states while behavior this system toward partial oxidation of methanol is mainly dependent on surface texture, solid-solid interaction between active phase and support. The results revealed that the catalytic activity of nanosized FeMgO system toward H_2O_2 decomposition follows the sequence as: $FeMgO_{HY} > FeMgO_{Co} > FeMgO_{IM}.$ While behavior this system toward partial oxidation of methanol can be ranked as: FeMgO-_{Co} > FeMgO_{IM} > FeMgO_{HY}.

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