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Sol–Gel Synthesis of MoO_3/SiO_2 Composite for Catalytic Application in Condensation of Anisole with Paraformaldehyde

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Abstract MoO_3/SiO_2 composite with varying amounts of MoO_3 loading (1–20 wt.%) were prepared by sol–gel method and calcined at 500 °C. These catalysts were employed for the liquid phase condensation of anisole with paraformaldehyde. All the catalysts were characterized by N_2 sorption, XRD, and NH_3-TPD. The activities of synthesized MoO_3/SiO_2 catalysts were compared with *p*-toluene sulfonic acid (*p*-TSA), the most frequently used catalyst for the condensation reactions, and with a supported metal oxide (WO_x/ZrO_2). Under the similar reaction conditions, synthesized 10 wt.% MoO_3/SiO_2 catalyst calcined at 500 °C was found to be the most active in the condensation of anisole with paraformaldehyde.

Keywords Condensation of anisole · Paraformaldehyde · 4,4′-Dimethoxydiphenylmethane · Sol–gel synthesis · MoO_3/SiO_2 composites

1 Introduction

Molybdenum oxide as such or in supported form is widely used as catalysts in a great number of reactions. Particularly, molybdenum oxide supported on silica is a well-known solid acid catalyst, which possesses both strong Lewis and Bronsted acidity [1, 2]. Recently supported molybdenum oxide has attracted much attention for its use as solid acid catalysts [3–7], especially for dehydration, dehydrogenation, isomerization, and transesterification. The catalytic activity of supported molybdenum oxide depends on the degree of dispersion and structure of the supported phase. Therefore, the activity and the selectivity have been related to the nature of the active phase, which itself depends on the nature of the support, the molybdenum loading and also the preparation method. Although, most of the researchers [7, 8] use impregnation method but recently some groups report the use of the sol–gel method as an alternative and superior route to the impregnation method for preparing well dispersed MoO_3/SiO_2 catalysts [9–11]. Smith et al. [12] has reported the effect of the nature of surface species on the activity and selectivity of MoO_3/SiO_2 catalysts for the partial oxidation of methane to formaldehyde.

Condensation reactions of aromatic compounds are important because the products of these reactions are used in many industries. For example, bisphenols, the condensation products of phenols and formaldehyde and its derivatives, are used as chemicals and/or intermediates for the preparation of industrially useful epoxy resins, phenolic resins, polycarbonates, in the molding, casting, sealing, coating, encapsulating, adhesives, laminating, reinforced plastics, and other industrial chemicals [13]. Derivatives of 4,4′-dimethoxydiphenyl methane (4,4′-DMDPM) are used in the manufacture of polymer products [14, 15].

A wide range of condensation reaction has been studied using *p*-toluenesulfonic acid (*p*-TSA) as a catalyst [16–21]. Due to the problem in recovery of the catalyst and formation of large amount of waste, this process is environmentally unacceptable. Liquid phase condensation of anisole with paraformaldehyde over benzylsulfonic acid functionalized mesoporous Zr-TMS catalyst has been studied extensively by Chidambaram et al. but the anisole conversion was low [22].

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Considering the industrial importance of the reaction and product, we have prepared MoO_3/SiO_2 composites by sol–gel method, and applied in anisole condensation with paraformaldehyde as a liquid phase reaction in the absence of the solvent. The results are presented in this paper.

2 Experimental

2.1 Chemicals

Ammonium molybdate, tetraethyl orthosilicate (98%), propan-2-ol, anisole, and paraformaldehyde were procured from Qualigens Fine Chemicals, India Ltd., Mumbai, Aldrich Chemical Company, Inc., Ranbaxy Fine Chemicals Ltd., New Delhi, Loba Chemie Pvt. Ltd., Mumbai and Thomas Baker (Chemicals) Pvt. Ltd., Mumbai, India, respectively. All the chemicals were of research grade and were used as received without further purification.

2.2 Catalyst Preparation

MoO_3/SiO_2 catalysts with varying amounts of MoO_3 loading (1–20 wt.%), were synthesized by sol–gel method by modification of the literature procedure [10]. Ammonium molybdate and tetraethyl orthosilicate were used as molybdenum oxide and silica sources, respectively. In a typical synthesis of 1 wt.% MoO_3/SiO_2, 0.123 g ammonium molybdate was dissolved in hot 20 mL distilled water. This hot solution was added drop wise to the anhydrous isopropyl alcohol solution (20 mL) of tetraethyl orthosilicate (34.67 g) with constant stirring over a period of 30 min. After complete addition, the stirring was continued for additional 30 min. The obtained greenish mass was aged for 48 h at room temperature. The resultant gel was dried at 100 °C for 10 h and calcined at 500 °C in calcination furnace for 10 h. Similarly the catalysts with 5, 10, 15 and 20 wt.% molybdenum oxide loading were synthesized. Pure silica support was also prepared by adding 0.5 g of aq. ammonia solution (25%) to dry isopropyl alcohol solution (15 mL) of tetraethyl orthosilicate (25 g) with constant stirring. The resultant gel was aged, dried and calcined at 500 °C as mentioned above. The catalysts have been represented by x-MS-y [where: x = wt.% of (M = MoO_3) on (S = SiO_2) and y = calcination temperature in °C].

2.3 Catalyst Characterization

X-ray diffraction (XRD) patterns of MoO_3/SiO_2 composites were recorded on a Rigaku Geigerflex diffractometer equipped with Ni-filtered Cu-Kα radiation (λ = 1.5418 Å). The specific surface area of the catalysts were measured by N_2 physisorption at liquid nitrogen temperature using a Quanta chrome Nova-1200, surface area analyzer and standard multipoint BET analysis methods. Samples were degassed in flowing N_2 for 4 h at 200 °C before N_2 physisorption measurements. The total acidities of the catalysts were measured by temperature programmed desorption of NH_3 (NH_3-TPD) using a Micromeritics AutoChem-2910 instrument. It was carried out after 0.1 g of the catalyst sample dehydrated at 200 °C in He (30 cm^3 min^{-1}) for 2 h and the temperature was decreased to 100 °C, and NH_3 was adsorbed by exposing samples treated as above to a stream containing 10% NH_3 in He for 1 h at 100 °C. It was then flushed with He for another 1 h to remove physisorbed NH_3. The desorption of NH_3 was carried out in He flow (30 cm^3 min^{-1}) by increasing the temperature to 550 °C at the rate of 10 °C min^{-1} and measuring NH_3 desorbed using a TCD (thermal conductivity detector).

2.4 Reaction Procedure

The catalyst was activated at 200 °C for 5 h before its use in the experiments, so as to maintain the dry environment. In a typical run, a mixture of anisole (20 mmol), paraformaldehyde (10 mmol) and activated catalyst (0.15 g) was stirred in a 50 mL round bottom flask fitted with a condenser and heated in thermostated oil bath to attain the reaction temperature (90 °C). All the experiments were carried out in nitrogen environment. The reaction samples were withdrawn periodically, centrifuged and analyzed by Shimadzu 14B gas chromatograph, equipped with a flame ionization detector using HP-5 capillary column (cross linked 5% ME silicone, 30 m × 0.53 × 1.5 μm film thickness). The products were identified by GC-MS (QP-5000 Mass Spectrometer, GC-17A Gas Chromatograph) analysis. Conversions of anisole and product selectivities were calculated based on the gas chromatographic analysis.

3 Results and Discussion

3.1 Characterization of the Catalysts

The physico-chemical characteristics of the catalyst system are depicted in Table 1. The pure silica support showed a surface area of 450 m^2 g^{-1}. It is evident from the data that with the increase in MoO_3 loadings to the support, the specific surface area of catalysts decreased. This could be due to either the uncontrolled rate of hydrolysis or highly basic pH of the solution during sol–gel preparation. It was also expected that as MoO_3 loading increased, the crystalline molybdenum oxide clusters were formed covering the amorphous silica support and reducing the specific surface of the catalyst.

Table 1 Physico-chemical characteristics of MoO_3/SiO_2 catalysts

Entry	Catalyst	Surface area ($m^2\ g^{-1}$)	Acidity (mmol g^{-1})
1.	SiO_2-500	450	0.114
2.	1-MS-500	380	0.212
3.	5-MS-500	215	0.903
4.	10-MS-500	182	1.614
5.	15-MS-500	135	1.426
6.	20-MS-500	86	1.100
7.	10-MS-400	–	0.631
8.	10-MS-600	–	1.157

Ammonia-TPD experiments were performed to determine the strength of acid sites present on the catalyst surface, together with total acidity. The results are given in Table 1. It is evident from the data that there is an initial increase in the acidity up to 10 wt.% of MoO_3 addition on the silica by sol–gel method, and thereafter the acidity decreases. The amount of ammonia desorbed for the pure silica support was 0.114 mmol g^{-1} showing the presence of few weaker acid sites, which became double (0.212 mmol g^{-1}) when 1 wt.% of MoO_3 was added to silica indicating the increase in number of acid sites and acid strength. The catalyst 10-MS-500 showed the highest acidity (NH_3 desorbed = 1.614 mmol g^{-1}) with maximum number of surface acid sites. For 10-MS catalyst calcined at different temperatures, the amount of desorbed ammonia increased with the increase in calcination temperature and reached a maximum at 500 °C. The development of acid sites was related to the coordinatively unsaturated Mo^{6+} species on the surface (Lewis acid sites) [23] and to the hydroxyl groups formed by protonating the bridging Si=O=Mo or terminal Mo=O bonds on the surface (Bronsted acid sites) of the samples [24, 25]. The decrease in the acidity at high calcinations temperature and high loading could be due to the formation of bulk Molybdenum oxide.

The diffraction patterns of the pure silica and 1–20 wt.% MoO_3/SiO_2 catalysts prepared by the sol–gel method and calcined at 500 °C are depicted in Fig. 1A. Pure silica and materials of low MoO_3 loading are found to be amorphous in nature (Fig. 1(A) a–c). Catalysts with 10 wt.% MoO_3 loading and above calcined 500 °C showed crystallinity of the materials with peaks at 2θ = 12.8, 23.4, 25.7 and 27.3° corresponding to orthorhombic phase of α-MoO_3. In case of 20-MS-500 sample (Fig. 1(A) f), the absence of the hump in the 2θ ranges of 20–30° due to amorphous silica is an indication of the formation of bulk molybdenum oxide phase. Similar observation has been made for the sample calcined at 600 °C (Fig. 1(B) c). The 400 °C calcined sample (Fig. 1(B) a) showed the silica hump as well as the small crystalline peaks of MoO_3 indicating the well dispersion of MoO_3 in the support. It is evident from the diffraction patterns of the catalysts there is a uniform distribution of MoO_3 in orthorhombic phase on the amorphous silica up to 10 wt.% loading and calcined at 500 °C (Fig. 1(A) d) and with the higher MoO_3 loading and the higher calcinations temperature MoO_3 becomes the bulk phase which can be correlated with the catalytic activity of the material. Same trend on the increased loading of MoO_3 was reported in the literature [12], according to these authors, a highly dispersed silicomolybdic species with terminal Mo=O sites exist for low MoO_3 loadings. As the molybdenum content is increased, these sites are transformed into polymolybdate species, forming Mo–O–Mo bridging sites at the expense of Mo=O sites. Finally, crystalline MoO_3 is detected at high molybdenum contents.

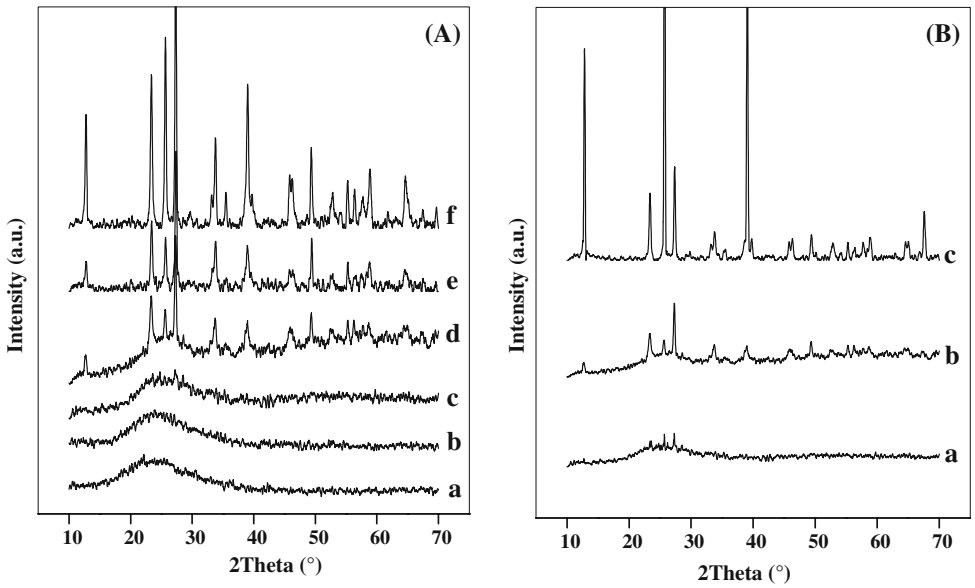
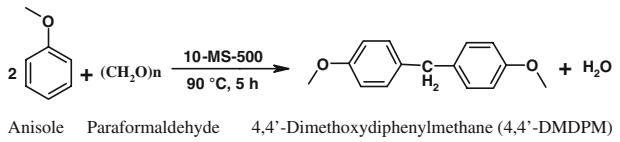


Fig. 1 XRD patterns of (**A**) catalysts with different MoO_3 loadings (a) silica, (b) 1-MS-500, (c) 5-MS-500, (d) 10-MS-500, (e) 15-MS-500, (f) 20-MS-500 and (**B**) 10-MS-500 calcined at different temperatures (a) 10-MS-400, (b) 10-MS-500, (c) 10-MS-600



Scheme 1 Condensation of anisole with paraformaldehyde

3.2 Catalytic Activity Determination

Condensation of anisole with paraformaldehyde catalyzed by MoO_3/SiO_2 (Scheme 1) at 90 °C resulted in the formation of desired product 4,4′-DMDPM, small amount of 2,4′-DMDPM and comparatively very small amount of 2,2′-DMDPM. WO_x/ZrO_2 (prepared as reported in [26], Entry 10, Table 2) was also found to be active showing 55 wt.% anisole conversion but this was comparatively lower than that showed by 10-MS-500 (71 wt.%, Entry 4, Table 2). *p*-TSA, a homogeneous catalyst showed high activity (75 wt.% anisole conversion) but low selectivity (66%) of the desired product (Entry 9, Table 2). Maximum conversion of anisole (71 wt.%) was achieved using 10-MS-500 catalyst with 90% 4,4′-DMDPM selectivity. The catalyst calcined at different temperatures showed lower activities in comparison with 10-MS-500, which could be due to the higher acidity of the 10-MS-500. The XRD pattern of 10-MS-500 catalyst showed the uniform distribution of MoO_3 species on SiO_2 support and also the orthorhombic phase which might be responsible for its higher activity. Among all the catalysts under study, 10-MS-500 catalyst was found to be the most active and selective.

3.3 Study of the Effects of Various Reaction Parameters

The effects of reaction parameters such as temperature, anisole to paraformaldehyde molar ratio, time and amount of catalyst were investigated on the conversion of anisole and product selectivity. In the first set of experiments, we have tried to study the effect of reaction time on the conversion of anisole and the product selectivity using 10-MS-500 catalyst at 90 °C and the results were presented in Fig. 2. The conversion of anisole increased steadily up to 15 h and then reached almost its steady state. The reaction gave mainly 4,4′-DMDPM with 90% selectivity. The results demonstrate that there was no significant effect of reaction time on 4,4′-DMDPM selectivity.

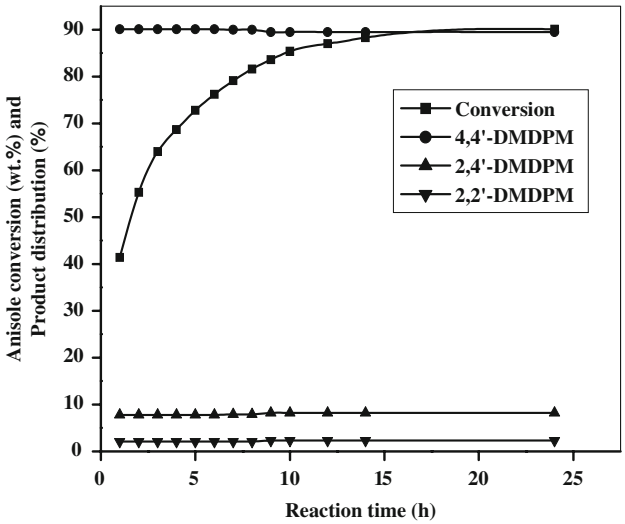


Fig. 2 Effect of reaction time on the conversion of anisole (wt.%) and product distribution (%). Reaction conditions: catalyst, 10-MS-500, (g) = 0.15; anisole (mmol) = 20; paraformaldehyde (mmol) = 10 and temperature (°C) = 90

In the next set, the effect of reaction temperature in the conversion of anisole and the product selectivity using 10-MS-500 catalyst was studied. It was seen from Fig. 3 that with increase in the temperature from 70 to 100 °C, the conversion of anisole increased from 44 to 79 wt.%. However, the selectivity of 4,4′-DMDPM remained nearly unaltered with the increase in reaction temperature.

The study of the effect of anisole to paraformaldehyde molar ratio on the conversion of anisole and the product

Table 2 Catalytic activity of various catalysts[a]

Entry	Catalysts	Conversion of anisole (wt.%)	Product distribution (%)			
			4,4′-DMDPM	2,4′-DMDPM	2,2′-DMDPM	Others
1.	SiO_2-500	5	90	8	2	–
2.	1-MS-500	20	90	8	2	–
3.	5-MS-500	44	90	8	2	–
4.	10-MS-500	71	90	8	2	–
5.	15-MS-500	60	90	8	2	–
6.	20-MS-500	45	89	9	2	–
7.	10-MS-400	44	89	9	2	–
8.	10-MS-600	51	88	9	3	–
9.	*p*-TSA	75	66	15	6	13
10.	15 wt.%WO_x/ZrO_2	55	70	22	8	–

[a] Reaction conditions: anisole (mmol) = 20; paraformaldehyde (mmol) = 10; catalyst (g) = 0.15; temperature (°C) = 90 and time (h) = 5

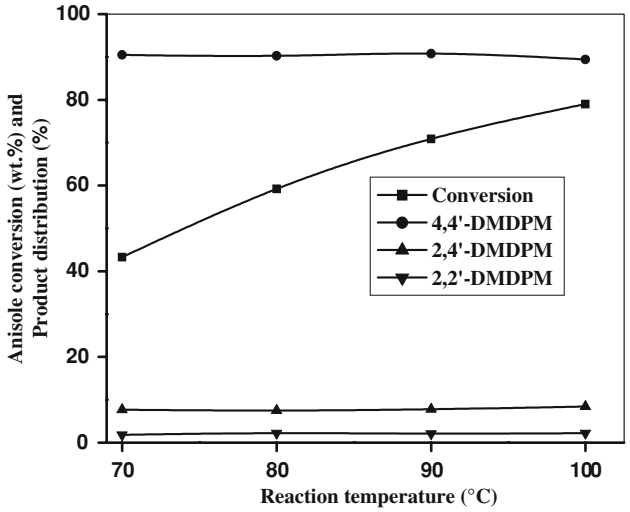


Fig. 3 Effect of different reaction temperatures on the conversion of anisole (wt.%) and the product distribution (%). Reaction conditions: catalyst, 10-MS-500, (g) = 0.15; anisole (mmol) = 20; paraformaldehyde (mmol) = 10 and reaction time (h) = 5

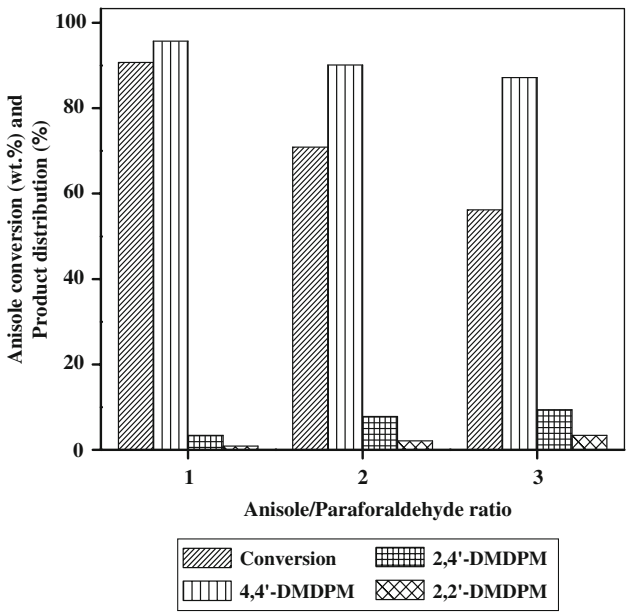


Fig. 4 Effect of anisole to paraformaldehyde molar ratio on the conversion of anisole (wt.%) and the product distribution (%). Reaction conditions: catalyst, 10-MS-500, (g) = 0.15; anisole (mmol) = 10, 20, 30; paraformaldehyde (mmol) = 10; temperature (°C) = 90 and reaction time (h) = 5

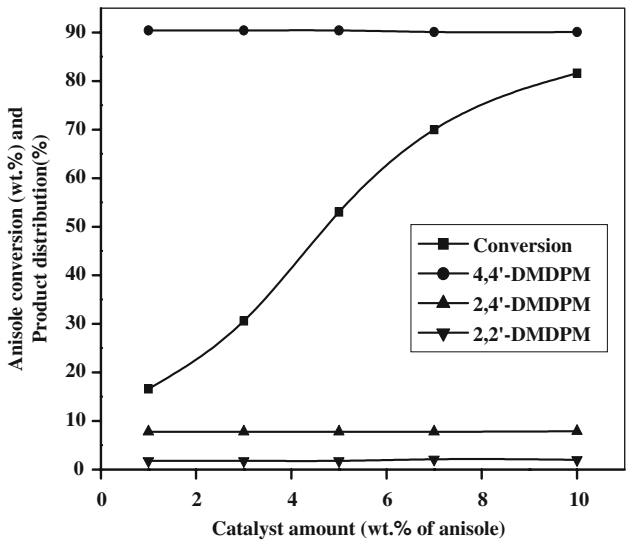


Fig. 5 Effect of amount of catalysts on the conversion of anisole (wt.%) and the product distribution (%). Reaction conditions: catalyst, 10-MS-500, (wt.% of anisole) = 1–10; anisole (mmol) = 20; paraformaldehyde (mmol) = 10; temperature (°C) = 90 and reaction time (h) = 5

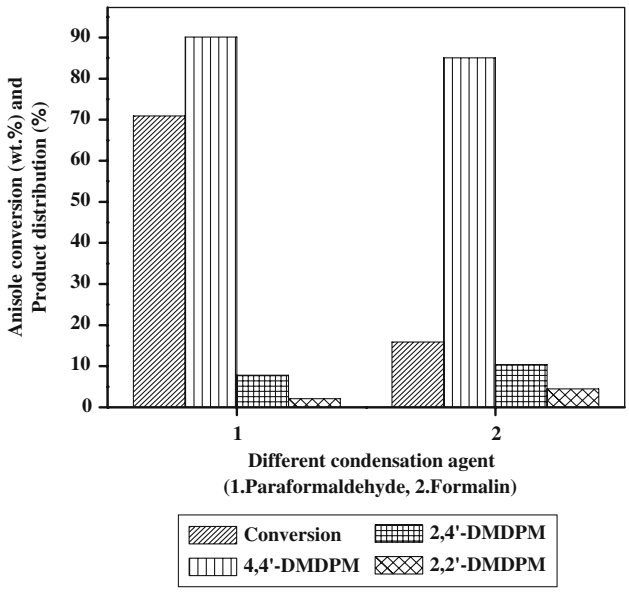


Fig. 6 Effect of different condensation agents on the conversion of anisole (wt.%) and product distribution (%). Reaction conditions: catalyst, 10-MS-500, (g) = 0.15; anisole (mmol) = 20; paraformaldehyde/formalin (mmol) = 10; temperature (°C) = 90 and reaction time (h) = 5

selectivity has been carried out and the results were shown in Fig. 4. The reaction data clarified that, as anisole to paraformaldehyde molar ratio increased from 1 to 3, the conversion of anisole decreased from 91 to 56 wt.%. Also, the selectivity to 4,4′-DMDPM was found to decreased with the increased in molar ratio. Thus, from the above observations, maximum conversion of anisole and selectivity to 4,4′-DMDPM could be obtained with 1:1 molar ratio (anisole:paraformaldehyde).

The effect of amount of catalyst (wt.% of anisole) on the conversion of anisole and product distribution was studied (Fig. 5). The amount of catalyst was increased from 1 to 10 wt.% of anisole keeping other conditions constant. The conversion of anisole increased from 18 to 82 wt.% as the

Table 3 Recyclability study of catalyst[a]

Entry	Cycle	Conversion of anisole (wt.%)	Product distribution (%)		
			4,4′-DMDPM	2,4′-DMDPM	2,2′-DMDPM
1.	Fresh	71	90	8	2
2.	1st recycle	69	89	8	3
3.	2nd recycle	66	87	9	4
4.	3rd recycle	62	85	11	4

[a] Reaction conditions: anisole (mmol) = 20; paraformaldehyde (mmol) = 10; catalyst, 10-MS-500, (g) = 0.15; temperature (°C) = 90 and time (h) = 5

amount of catalyst increased from 1 to 10 wt.%. However, the product distribution was found to be unaltered when the catalyst amount has changed. It can be seen (Fig. 5) that amount of catalyst in the reaction mixture had a great effect on conversion of anisole. A quick enhancement in conversion of anisole was seen with the increase in catalyst amount from 3 to 7 wt.%. Thus by using catalyst amount = 7 wt.% of anisole, the conversion of anisole and selectivity to 4,4′-DMDPM were found to be 71 wt.% and 90%, respectively.

The condensation reaction was also performed using different condensing agents, formalin (aq. formaldehyde, 37–41%) and paraformaldehyde (Fig. 6). The lower anisole conversion (16 wt.%) was obtained with formalin as compared with that of paraformaldehyde (71 wt.%). Since the formalin contains the high concentration of water, the active species of the catalyst may leach out from the surface of the support. On the other hand, paraformaldehyde is in the polymeric form, it decomposes at higher temperatures and gives the monomer, takes part, in the catalytic reaction. Small amount of water formed as a byproduct of the condensation, this dissolved the polymeric paraformaldehyde and as a result the monomers formed took part in reaction and enhance the conversion of anisole. Thus, paraformaldehyde is a suitable condensing agent compared to formalin.

3.4 Recyclability Study of Catalyst

One of the main advantages of using solid catalyst in the liquid phase reaction is the ease of separation and reuse in subsequent catalytic cycles. The repeated use of 10-MS-500 catalyst was carried out for three times (fresh + three cycles) in the reaction under study (Table 3). After the completion of reaction, the separation of the catalyst was done by the filtration, washing with water and acetone and then the obtained catalyst was dried at 100 °C for 5 h and recalcined at 500 °C for 10 h. A marginal decrease in anisole conversion was observed when the catalyst was used in 1st, 2nd and 3rd cycles which could be due to the slight leaching of the active species from the surface due to formation of water as a byproduct in the reaction and due the use of water for the separation of the catalyst from the reaction mixture. However, the selectivity to 4,4′-DMDPM decreased from 90% to 85%.

4 Conclusions

The condensation of anisole with paraformaldehyde catalyzed by MoO_3/SiO_2 composite prepared by sol–gel method gave mainly 4,4′-DMDPM. The activity of MoO_3/SiO_2 catalyst has been compared with the known catalysts like *p*-TSA and WO_x/ZrO_2. Under the similar reaction conditions, synthesized 10-MS-500 was found to be the best among the catalysts studied, which is attributed to its highest acidity and uniform distribution of MoO_3 species on silica support. The conversion of anisole catalyzed by 10-MS-500 dependent strongly on reaction conditions and increased greatly with time, temperature, amount of catalyst, while decreased with increase in anisole to paraformaldehyde molar ratio. The proposed catalyst system prepared by sol–gel method is easy to prepare and it could be recycled without significant loss in its activity.

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