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Oxidation of Cyclohexene Catalyzed by PAMAM-SA-M Dendrimers

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Abstract: Oxidation of cyclohexene under 1 atmospheric pressure of molecular oxygen at 70°C in the absence of solvent catalyzed by PAMAM-SA-M (Where PAMAM = polyamidoamine; SA = salicyaldehyde; M = metal ions Fe^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, respectively) dendrimers, afforded 2-cyclohexen-1-ol **1,** 2-cyclohexen-1-one **2,** 7-oxabicyclo [4,1,0] heptane **3** and 7-oxabicyl [4,1,0] heptan-2-one **4** as the major products. The factors that affect this reaction are also discussed.

Keywords: Dendrimer, coordination, catalysis, oxidation, cyclohexene.

Over the last twenty years, much interest has concentrated on the study of dendrimers[1-3]. Their highly symmetrical molecular structure and many special properties, such as the general ease of construction, the well-behaved water-soluble features, ensure that these compounds will be of very useful materials for many promising future uses. This paper reports the synthesis and catalytic oxidation properties of a series of metal containing dendrimers which were obtained through the PAMAM dendrimer (PAMAM = polyamidoamine)[4], through modification of its peripheral groups with lower molecular weight organic molecules and subsequently coordinate with a variety of metal ions. As we had expected, the reactions have generated some exciting results, which are described herein.

The dendrimer PAMAM (G=1) was prepared according to the literature[4]. In summary, a condensation reaction between PAMAM and SA gave a Schiff base PAMAM-SA and the metal containing dendrimers were obtained through the reaction of this Schiff base with the corresponding metal ions of Fe^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+} and Zn^{2+}, respectively. Each dendrimer was fully characterized by IR, UV, NMR, ICP and elemental analysis. The dendritic structures (**Scheme 1**, G=3) and the probable coordination patterns of the metal containing dendrimers (**Scheme 2**, G=3) are shown below.

A series of oxidation reactions were carried out to evaluate the catalytic activity of these newly synthesized dendrimers. The oxidation reaction of substrate cyclohexene, under 1 atmospheric pressure of molecular oxygen at 70°C in the absence of solvent, was

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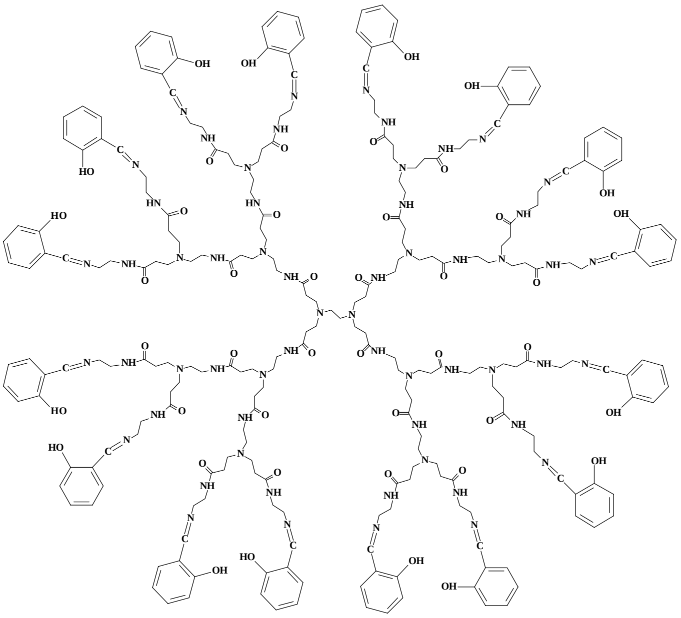
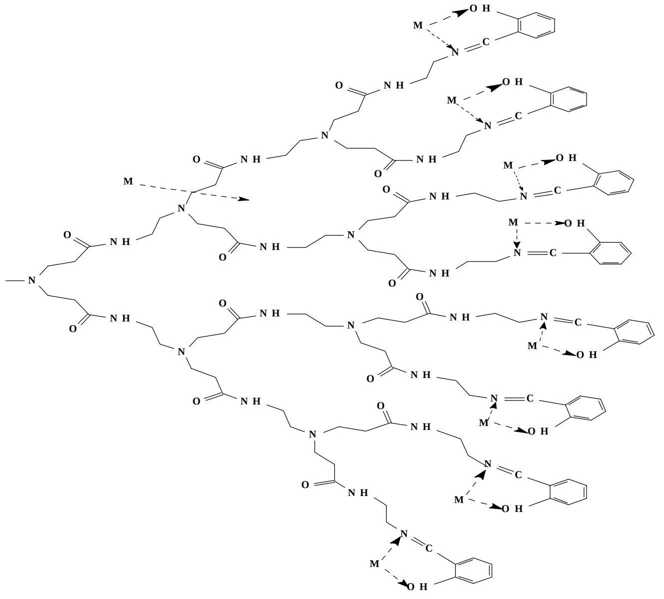
chosen for this study. In each case, 2-cyclohexen-1-ol **1,** 2-cyclohexen-1-one **2,** 7-oxabicyclo[4,1,0] heptane **3** and 7-oxabicyl[4,1,0] heptan-2-one **4** were obtained as the major products (determined by GC/MS, column: 5m × 3mm OV-101) as follows (**Scheme 3**).

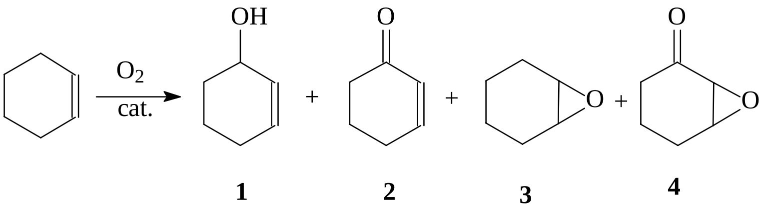
Scheme 1



Seheme 2



Scheme 3



The speed of oxygen consumption and the selectivity of the catalysts are shown in **Table 1**.

Table 1 The results of the oxidation catalyzed by PAMAM-SA-M (G=1) dendrimers

Catalyst	Oxygen consumed (mL / mol cat s)	Yield of products (%)				
		1	**2**	**3**	**4**	Total
PAMAM-SA-Fe^{3+}	3.79×10^7	24.29	24.63	5.99	37.63	71.5
PAMAM-SA-Co^{2+}	1.85×10^7	21.89	24.26	6.26	36.11	70.5
PAMAM-SA-Ni^{2+}	1.60×10^7	25.87	19.67	7.17	47.87	72.1
PAMAM-SA-Mn^{2+}	1.58×10^7	24.81	26.66	7.73	41.49	75.8
PAMAM-SA-Cu^{2+}	2.56×10^7	42.88	43.49	6.56	7.18	92.9
PAMAM-SA-Zn^{2+}	2.12×10^7	14.16	11.64	7.08	64.12	84.8

Reaction condition: cat. 1 mg, cyclohexene 5 mL, 1 atmospheric pressure of O_2, 6 h, and 70°C.

Table 1 shows that the reactivity and oxidation selectivity of the catalysts were changed considerably. Fe^{3+} and Cu^{2+} complexes have higher catalytic reactivity, but the selectivity to **4** is relatively low. Contrastingly, the Ni^{2+} complex possesses lower reactivity under the same condition, but give higher selectivity for product **4**. Especially for the Zn^{2+} complex, its selectivity to product **4** is about 65%. This is the first reported on synthesis of product **4** *via* this type of oxidative reaction using the dendritic catalysts. Since the product of **4** can be used as a useful intermediate for the organic synthesis, it is likely that this type of oxidative reaction will be especially useful.

The ratio of the catalyst to the substrate is a major factor on the outcome of the oxidation reaction. For example, concerning to the Mn^{2+} complex, when the ratio of substrate/catalyst is 5 mL/1 mg, its oxygen consuming is 1.58×10^7 mL/mol cats, when the substrate/catalyst changed to 5 mL/2 mg, 5 mL/0.5 mg, the oxygen consuming rate was 2.22×10^7 mL/mol cats, 1.90×10^7 mL/mol cats, respectively.

Another factor that affects catalytic reactivity and selectivity is dendritic generation. For example, when the ratio of substrate/catalyst is 5 mL/1 mg, the PAMAM-SA-Ni^{2+} (G=1) has the oxygen consuming of 1.60×10^7 mL/mol cats, while the PAMAM-SA-Ni^{2+} (G=2) is 3.48×10^7 mL/mol cats, the PAMAM-SA-Ni^{2+} (G=3) is 2.89×10^7 mL/mol cats. The reason for this result is still not clear.

Resulting from the special molecular structure and the unique properties of the dendrimer, the reactions were essentially carried out under heterogeneous condition. These reagents not only can be used for some solid phase organic synthesis but also some of them can be readily recycled. This property of these catalysts is significant for the environmental protection, because some of them contain the hazardous metal.

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