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Liquid Phase Oxidation of Aniline over Various Transition-Metal-Substituted Molecular Sieves

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The oxidation of aniline has been performed in the liquid phase at moderate temperatures over a series of transition-metal-substituted molecular sieves. Experimental data have shown that TS-1 was not the best catalyst for this reaction but that large pore zeolites or mesoporous silicas were preferred. Indeed, these solids could be used with either hydrogen peroxide or *tert*-butyl hydroperoxide (TBHP) as oxidant. For low oxidant/aniline ratios, azoxybenzene (AZY) was the major product formed over Ti-containing catalysts, but azobenzene (AZO) and nitrosobenzene (NSB) were also detected. The selectivity in AZO was always higher with TBHP than with H_2O_2. In contrast, V-substituted zeolites were only active with TBHP and led to the very selective formation of nitrobenzene. © 1995 Academic Press, Inc.

INTRODUCTION

The oxidation of aniline and more generally arylamines is an important reaction for fundamental and industrial applications. Therefore, it has attracted considerable attention during the past 2 decades. The practical interest of O-containing derivatives of aniline is due to their use in several fields as chemical or pharmaceutical products (1, 2). Even though many industrial routes have been reported to prepare these compounds, most of them are noncatalytic routes and lead to the formation of large amounts of inorganic polluting effluents. Different reagents such as peracetic acid (3), MnO_2 (4), $Pd(OAc)_4$ (5), or $Hg(OAc)_2$ (6) have been used.

Homogeneous catalytic oxidations have also been carried out using soluble salts of transition metal cations like Ti^{4+} (7), V^{4+} (8), Mo^{6+} (8, 9), or Fe^{3+} (10, 11). Most of these reactions led to the selective formation of azoxybenzene (AZY) with hydrogen peroxide and nitrobenzene (NB) with *tert*-butyl hydroperoxide (TBHP). Nitrosobenzene (NSB) could also be formed selectively with H_2O_2.

In view of the current interest in environmental protection, we have been working in the development of heterogeneous catalysts for aniline and arylamines oxidation.

We have recently reported (12), almost simultaneously with Sonawane *et al.* (13), that TS-1, the titanium-substituted silicalite-1, could be an excellent catalyst for the selective oxidation of aniline to azoxybenzene. Sonawane *et al.* (13) gave only few details about the reaction and about the nature of the products formed. In contrast, we reported a detailed study of the reaction. We have particularly shown that:

— Aniline could be selectively oxidized to azoxybenzene over TS-1 with a selectivity of 95% in AZY for a H_2O_2 conversion of about 100%;

— Nitrosobenzene was formed at the beginning of the reaction and was slowly transformed as the reaction progressed.

Based upon experimental observations, we concluded that the formation of phenylhydroxylamine (PH) (and maybe NSB) most likely occurred inside the TS-1 channels. In contrast, AZY was probably formed in the solution, by reaction of NSB with the very unstable PH.

Depending on the initial H_2O_2 concentration, nitrobenzene could also be formed, probably from the oxidation of NSB. However, as far as the H_2O_2/aniline ratio did not exceed 1, this product was not detected.

Experiments carried out on a series of catalysts having various crystal sizes have shown that the reaction was limited by the diffusion of products and/or reagents in the zeolite pores. Similar conclusions could be derived from the data of Sonawane et al. (13) concerning the oxidation of substituted anilines.

In the present paper, we report on the oxidation of aniline over various molecular sieves, using several alkylperoxides as oxidant. It is indeed well known that TS-1 is not the only zeolite capable of catalyzing oxidation reactions in the presence of dilute H_2O_2. We have thus synthesized a series of transition-metal-substituted molecular sieves and examined the role of the pore diameter, the dimensionality of the channel system and that of the nature

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of the oxidant. We also report details about the influence of the nature of the incorporated metal and its concentration in the molecular sieve. Finally, the effect of varying the oxidant/substrate ratio on the catalyst performance is discussed.

EXPERIMENTAL

Syntheses

Various TS-1 samples were synthesized following example 1 of the original patent (14), using tetraethyl orthosilicate (Aldrich, 98%), tetraethyl orthotitanate (Aldrich, 99%), and alkali-free tetrapropylammonium hydroxide solutions (TPAOH).

VS-1, the vanadium-substituted silicalite-1, was obtained by changing TEOT with an aqueous solution of $VOSO_4 \cdot 5H_2O$ in the synthesis of TS-1.

Various Ti-Beta zeolites were synthesized following a route slightly different from that of the literature (15, 16). TEOS was first hydrolyzed with a solution of tetraethylammonium hydroxyde (TEAOH). Then tetrabutyl orthotitanate in dry isopropyl alcohol was added, and the mixture was stirred for about 20 min. Distilled water and aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O$, Aldrich) were then added, and the resulting liquid was crystallized at 140°C for 5 days under static conditions.

A titanium containing SAPO-5 (TAPSO-5) was obtained following a very recently reported method (17).

[Ti]ZSM-48 (TS-48) was prepared using trimethylpropylammonium hydroxide solutions, as recently published in the literature (18).

An amorphous Ti supported silica was obtained by reaction of TiF_4 with SiO_2 (19). This method allowed us to obtain highly dispersed Ti^{4+} ions on various supports.

Ti-containing mesoporous silica (Ti-HMS) was synthesized following a recipe recently given by Tanev *et al.* (20). Dodecylamine was used as a surfactant templating molecule and led to the formation of uniform mesopores of about 28 Å in diameter. V-HMS, the vanadium-substituted mesoporous silica, was synthesized following the same recipe but using vanadyl acetylacetonate instead of titanium isopropylate as the metal precursor.

Ti-MCM 41 was synthesized at 105°C with cetyltrimethylammonium cations and Ludox AS-40 (DuPont) following the recipe given by Rathousky *et al.* (21).

Finally, VAPO-5 was prepared using an alkaline synthesis route with pseudoboehmite (CATAPAL B, Vista), orthophosphoric acid (RP Normapur, 85 wt%), vanadium pentoxide, and tripropylamine (22).

Characterization

The structure of the different zeolites was characterized by X-ray diffraction (Philips PW 1710) and infrared spectroscopy (Perkin Elmer 580) using the KBr method (1 wt% zeolite in KBr). The location and coordination of heteroatoms in the framework were given by UV–Vis spectroscopy and EPR spectroscopy (Varian E9, X-band mode) for vanadium.

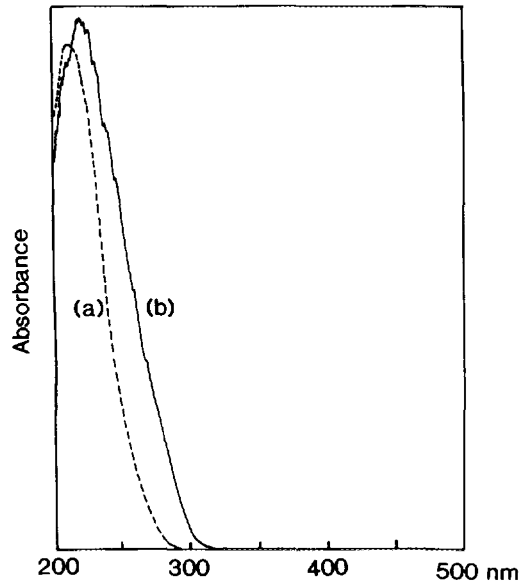


FIG. 1. Diffuse reflectance UV–vis spectra of (a) TS-1 (sample 1) and (b) Ti-HMS (sample 8).

Chemical analyses were obtained by atomic absorption after solubilization of the samples in HF/HCl solutions.

Catalytic Reactions

The catalytic oxidation of aniline (Aldrich, 99%) was performed in a round-bottomed flask equipped with a condenser and a magnetic stirrer. In a typical reaction, 0.5 g of catalyst was dispersed in a solution containing 20 ml of solvent and 4.6 ml of aniline. The mixture was stirred at 70°C, and the required amount of alkyl peroxide was then added in one lot.

Samples were periodically taken and analyzed by gas chromatography using a nickel column (2 m × $\frac{1}{8}$ in.) packed with Tenax GC 60/80 (Alltech). This column was attached to a chromatograph (GC 121 FB, Delsi) fitted with a F.I.D. The temperature of the column was 270°C and those of the injector and the detector were 300°C.

RESULTS AND DISCUSSION

For all catalysts (except Ti-supported silica and the mesoporous materials), the structure and crystallinity were examined by X-ray diffraction and IR spectroscopy. The absence of extraframework oxide species was confirmed by UV–vis spectroscopy. As an example, Fig. 1 shows the diffuse reflectance UV–Vis spectra of TS-1, Ti-Beta, and

TABLE 1

Characteristics of the Different Catalysts

No.	Catalyst	Si/Me	Si/Al	Φ(Å)	*D*
1	TS-1	85	∞	5.6	3
2	VS-1	123	∞	5.6	3
3	TS-48	107	∞	5.6	1
4	TAPSO-5	94[a]	—	7.3	1
5	Ti-Beta	112	19	7.6	3
6	Ti-Beta	87	85	7.6	3
7	Ti-Beta	98	137	7.6	3
8	Ti-HMS	85	∞	28	1
9	Ti MCM-41	92	∞	34	1
10	V-HMS	108	∞	28	1
11	VAPO-5	97[b]	—	7.3	1
12	Ti-HMS	45	∞	28	1
13	Ti-HMS	31	∞	28	1
14	V-HMS	62	∞	28	1
15	V-HMS	36	∞	28	1

Note. Φ(Å) is the mean pore diameter and *D* is the dimensionality of the zeolite channel system.

[a] (Si + Al + P)/Ti.

[b] (Al + P)/V.

Ti-HMS, all samples being prepared with Si/Ti = 100 in the precursor gel. Peaks in the 330-nm region were never observed, confirming the absence of TiO_2 particles (23). For TS-1 and Ti-Beta, the UV absorption edge is around 210 nm, typical of Ti^{4+} cations in a tetrahedral coordination. The absorption band is broader for Ti-HMS and the edge shifted to about 230 nm. This agrees very well with previous observations indicating that Ti atoms in titanium-containing mesoporous silicas would rather be in an octahedral coordination (24).

The chemical composition as well as the structural characteristics of the samples are listed in Table 1. Catalysts could be classified according to the following:

- the pore diameter,
- the dimensionality of the channel system, and
- the nature of the incorporated metal.

For 3-dimensional channel systems, pore diameters increaed from TS-1 to Ti-Beta. In the case of 1-D zeolites, the order was ZSM-48 < TAPSO-5 < Ti-HMS. For similar pore diameters, the channel dimensionality increased from [Ti]ZSM-48 to TS-1 and from TAPSO-5 to Ti-Beta.

Except for TS-1 and Ti-HMS (where various samples were synthesized) all catalysts contained about the same Ti content.

I. Oxidations with Aqueous H_2O_2

Influence of the pore diameter. Figure 2 shows the yields in AZY and NSB obtained over TS-1 (sample 1) and a Ti-Beta sample (Si/Al = 19, sample 5). Reactions were performed in acetonitrile with an initial concentration in H_2O_2 corresponding to H_2O_2/aniline = 0.2. Both zeolites had a 3-dimensional channel network, but the pore diameter of zeolite Beta (≈7 Å) was larger than that of TS-1. The rate of formation of AZY was higher over Ti-Beta. NSB was only observed at the beginning of the reaction and rapidly transformed into AZY.

Figure 2 also shows the results of the oxidation of aniline over [Ti]ZSM-48 (sample 3), TAPSO-5 (sample 4), and Ti-HMS (sample 8). The rate of formation of AZY increased from [Ti]ZSM-48 to TAPSO-5 and Ti-HMS, i.e., with the pore diameter of the structure. Moreover, the activity was also very high over the amorphous Ti/SiO_2 catalyst, thus confirming that the formation of AZY was limited by diffusion over medium pore zeolites. Tanev *et al.* (20) have reported that a major difference betewen Ti-HMS and Ti MCM-41 was a higher textural mesopore volume for Ti-HMS. In particular, they showed that if the mesoporosity did not affect the activity of the catalyst in the oxidation of small substrates, it could drastically increase its preformances in the case of large substrates. When the oxidation of aniline is performed over Ti-MCM 41, the activity is very similar to that obtained over Ti-HMS, indicating that the textural mesoporosity of the catalyst does not greatly influence its behaviour under the working conditions. These results also show that the activity of Ti-containing mesoporous silicas is not significantly affected by the dimension of the mesopores, in contrast to what is observed with medium pore zeolites. All the results show that TS-1 is not a unique catalyst capable of oxidizing aniline with H_2O_2 at mild conditions. The nature

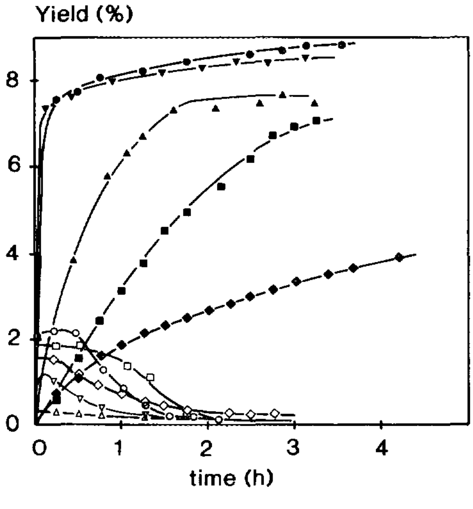


FIG. 2. Yield in azoxybenzene (filled symbols) and nitrosobenzene (open symbols) during the oxidation of aniline over various Ti-substituted molecular sieves: (●, ○) Ti-Beta (sample 5); (▼, ▽) Ti-HMS (sample 8); (▲, △) TS-1 (sample 1); (■, □) TAPSO-5 (sample 4); and (◆, ◇) TS-48 (sample 3). Reaction conditions: 0.5 g catalyst, H_2O_2/Aniline = 0.2, T = 70°C, solvent = acetonitrile

of the zeolite structure seems to be less critical than for hydroxylation reactions where only TS-1 and TS-2 are active. Nevertheless, the presence of isolated Ti atoms is necessary; indeed, TiO_2 as well as TiO_2-supported silicalite do not show good activities in the reaction.

Influence of the dimensionality. Figure 2 shows that TS-1 is more active than [Ti]ZSM-48 and that the rate of formation of AZY is higher over Ti-Beta than over TAPSO-5. All these results were not due to changes in the crystal size. Indeed, for the majority of the catalysts described above, the particle size was very small, particularly for [Ti]ZSM-48 where needles were about 1 μm length with less than 0.1 μm diameter. Variations in activity may also be explained by different Ti/Si ratios at the surface of the crystals. However, surface Ti/Si ratios obtained by XPS reflected quite well the bulk composition. Finally, these data clearly show that the reaction did not take place on the outer surface of the crystals alone. If this was the case, TS-1, [Ti]ZSM-48, and Ti-Beta, whose crystal sizes and Ti contents were similar, would not have shown such important differences in activity. Therefore, the results are in line with diffusion limitations of products and/or reagents inside the pores of the molecular sieves due to differences in the dimensionality of the zeolites.

Influence of the acidity of the catalyst. We have seen that Ti-Beta had an activity similar to that of Ti-HMS or Ti/SiO_2 in the oxidation of aniline with hydrogen peroxide. However, a major difference between Ti-Beta and the other two catalysts is that Ti-Beta contains large amounts of aluminium in the framework (Si/Al = 19) and thus possesses acidic properties. We have previously reported that incorporation of small amounts of aluminium in the framework of TS-1 led to a slight drop in the activity (12). However, we suspected a partial blocking of the zeolite pores due to the neutralization of the acid sites by aniline, thus hindering the real effects of the acidity. We have performed a series of catalytic reactions over various Ti-Beta zeolites, with Si/Al ratios from 19 to 139. In this case, the pore blocking observed over TS-1 was prevented by the relatively large dimensions of the zeolite channels.

Catalytic results are very interesting and show that Ti-Beta are very active for Si/Al ratios lower than 85 (Fig. 3). In this case, aniline is very rapidly and selectively oxidized to AZY. The nature of the products is similar to that obtained over aluminium-free catalysts like Ti-HMS.

For Si/Al = 137 (sample 7 prepared with Si/Al = 400 in the gel), the activity is comparable to that of a TS-1 having the same Ti content, but the H_2O_2 efficiency is relatively low (65% after 5 h of reaction). These results are surprising, as they suggest that aluminium could play a role in the catalytic oxidation of aniline. This is reinforced by the fact that the activity decreased when Al-rich Ti-Beta are exchanged with Na^+ cations. However, the lack of activity over acidic zeolites like pure Al-Beta (Si/Al < 50) or H-Y (Si/Al = 5) under the same experimental conditions refutes this hypothesis.

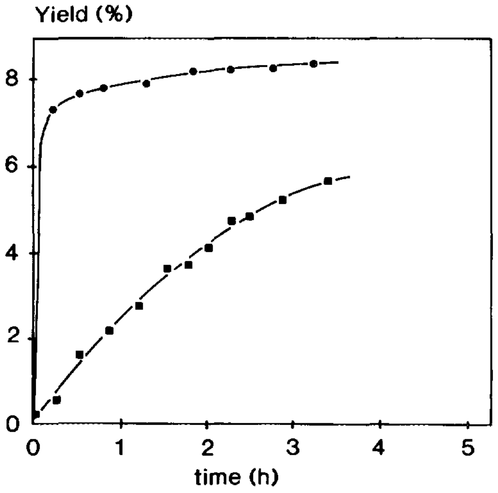


FIG. 3. Yield in azoxybenzene during the oxidation of aniline with hydrogen peroxide over various Ti-Beta catalysts: (●) sample 5 and (■) sample 7. For reaction conditions, see legend of Fig. 1.

A deeper examination of X-ray diffraction patterns of the samples reveals that sample 7 synthesized with Si/Al = 400 in the precursor gel has a lower crystallinity (76%) as compared to samples 5 and 6 (90% and 94%, respectively), which might explain at least partially the difference in activity. In the same manner, exchanging the H-catalysts with Na^+ cations probably reduces the accessibility to Ti active centers and thus decreases the catalytic performances. Therefore, the results show that the presence of acid sites in the catalysts do not change their activity in the oxidation of aniline with hydrogen peroxide.

Nature of the metal. Vanadium-substituted molecular sieves have also proved to be good catalysts for oxidation reactions in the liquid phase (25). When VS-1 was used instead of TS-1 in a standard reaction, no products were detected in significant amounts, even after several hours of reaction. VS-1 is known to be usually less active than TS-1 in most of the reactions. Nevertheless, Hari Prasad Rao *et al.* (26) have reported that the performance of the catalyst largely depended on the nature of the solvent.

We found that VS-1 was totally inactive in the oxidation of aniline with H_2O_2 when the reaction was performed either in water, *tert*-butanol, or acetonitrile. Surprisingly, V-HMS is also inactive under the same experimental conditions. Several reasons might be put forward to explain the lack of activity of these catalysts, for example, specific

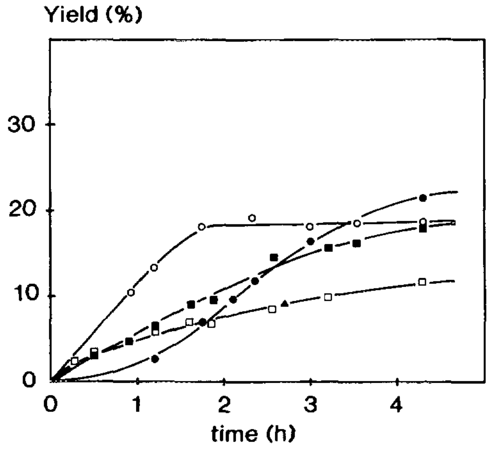


FIG. 4. Yield in azoxybenzene (black symbols) and azobenzene (white symbols) during the oxidation of aniline with *tert*-butyl hydroperoxide over various Ti-Beta catalysts: (●, ○) sample 5 and (■, □) sample 7. Reaction conditions: 0.5 g catalyst, TBHP/aniline = 2, T = 70°C, solvent = acetonitrile.

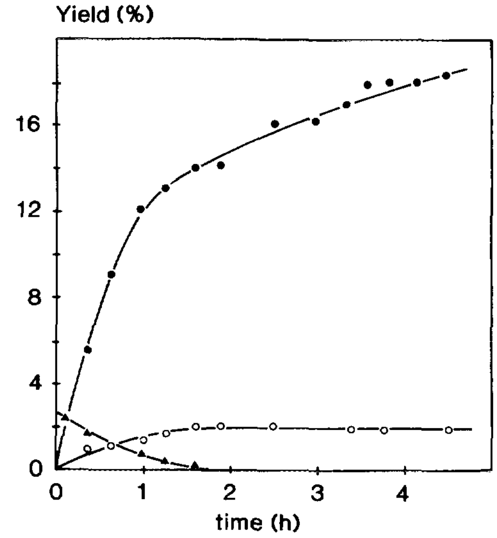


FIG. 5. Yield in (●) azoxybenzene, (○) azobenzene, and (▲) nitrosobenzene during the oxidation of aniline with TBHP over Ti-HMS (sample 8). Reaction conditions: 0.25 g catalyst, TBHP/aniline = 2, T = 70°C, solvent = acetonitrile.

interactions between aniline and vanadium sites of the zeolite or different mechanisms of reaction over Ti or V active sites. However, as reported below, V-HMS is very active in the oxidation of aniline to nitrobenzene with TBHP. The difference in behaviour between TS-1 and VS-1 in the presence of H_2O_2 is not yet clearly elucidated.

II. Oxidations with TBHP

All the reactions reported over TS-1 were performed with H_2O_2 as oxidant because TBHP was too large to enter the channels of the MFI structure. With the discovery of the large pore zeolite Ti-Beta, it has been possible to oxidize molecules with H_2O_2, particularly for epoxidation reactions. TBHP has also been used as oxidant in oxidation reactions over substituted molecular sieves such as VAPO-5 (27), CrAPO-5 (28), and very recently TAPSO-5 (17).

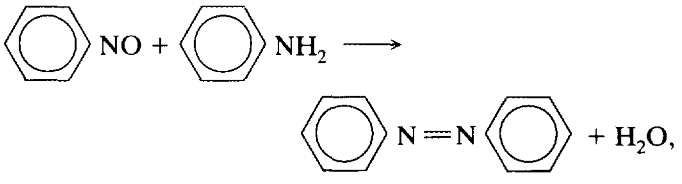
As expected, no conversion is observed with TBHP over medium pore zeolites like TS-1, VS-1, or [Ti]ZSM-48. Zeolites Ti-Beta with high Al contents have a relatively high activity for TBHP/aniline ratios > 2. In this case, the major products formed are AZY and AZO (Fig. 4). In contrast to reactions performed with H_2O_2, NSB is not detected, even at the very early stages of the reaction. The rate constant of formation of AZY measured under similar conditions (oxidant/substrate = 2, 0.25 g catalyst) is very low compared to that obtained with H_2O_2 over the same catalyst:

$$k(\mathrm{TBHP})/k(\mathrm{H_2O_2}) \approx 0.04.$$

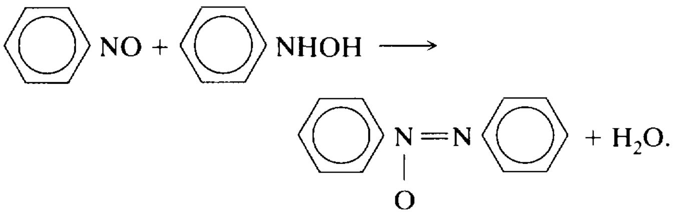
At the end of the reaction the selectivities are about 40% for AZO and 60% for AZY. The selectivity in AZY tends to increase with the Si/Al ratio of the zeolite. The TBHP efficiency, based upon the formation of AZO and AZY is about 58% for sample 5.

Neutralization of the acid sites of Ti-Beta zeolites with Na^+ cations does not only modify the activity of the catalyst. We also observe a slight increase in the AZY selectivity, thus suggesting that the acidity could play a role in the formation of AZO (Fig. 4).

Ti-substituted mesoporous silica is a very active catalyst in the oxidation of aniline with TBHP. Indeed, the alkyl peroxide can very easily penetrate the mesopores of the structure, which means that the reaction is not affected either by steric restrictions or by diffusion limitations. In contrast to Ti-Beta, Ti-HMS is active for all TBHP/aniline ratios. The influence of this ratio, i.e., the initial amount in peroxide, will be discussed later. For low TBHP/aniline ratios (<2.5), AZO and AZY were the major products formed, but NSB is also detected at the beginning of the reaction (Fig. 5). In contrast to Ti-Beta, the selectivity to AZO at the end of the reaction is relatively low (max 20%) over Ti-HMS. We have previously reported that AZO was probably formed by the reaction



whereas AZY was formed from the reaction of NSB on PH,



One explanation for the difference in AZO selectivities between Ti-Beta and Ti-HMS may be that AZO is probably formed in both cases, but is overoxidized over Ti-HMS. We had indeed reported that AZO could not be transformed into AZY over TS-1 because of the small pore opening of the structure. The problem is different over Ti-HMS were mesopores are about 28 Å in diameter. Therefore, we have carried out a reaction over Ti-HMS and Ti-Beta with AZO as the substrate. Over Ti-Beta, results are very similar to those previously reported over TS-1 (12); i.e., AZO is not converted to AZY in the presence of TBHP. As in the case of TS-1, this might be attributed to the relatively small pore opening of the zeolite. In contrast, more than 35% of AZO is transformed into AZY after 3 h over Ti-HMS (experimental conditions are the same as for the oxidation of aniline with TBHP), and that explains the lower AZO selectivity obtained over this catalyst.

Another reason for the presence of relatively large amounts of AZO when using TBHP as oxidant may be due to the metal-catalyzed decomposition of the peroxide to give radicals. In the oxidation of toluene with TBHP over VAPO-5, we have reported that products like dibenzyl were formed independently of the presence of the catalyst by reactions involving radicals (29). Similar considerations may explain the formation of AZO with TBHP, but the mechanisms are probably numerous and complex and not fully elucidated.

Reactions with TBHP were also performed over vanadium-substituted molecular sieves. It was already reported that VAPO-5 and CrAPO-5 were excellent catalysts for oxidation reactions with TBHP (27, 28). As far as the TBHP/aniline ratio is low (<1), no products are detected. For higher ratios, aniline is converted very selectively to nitrobenzene over VAPO-5 and V-HMS (Fig. 6). Traces of NSB are also observed but AZY is never obtained. The difference is very interesting even though the formation of NB from aniline is not interesting from an industrial point of view.

Using peroxotungstophosphates (PCWP), as heterogeneous catalysts, Sakaue *et al.* (2) observed that nitrobenzene was the product of further oxidation of NSB. In their system, the formation of NB required relatively large amounts of hydrogen peroxide or high temperatures. In fact, NB is formed when the catalyst possesses more active oxidant species. This is what we clearly observed when using V-HMS instead of Ti-HMS for similar TBHP/aniline ratios.

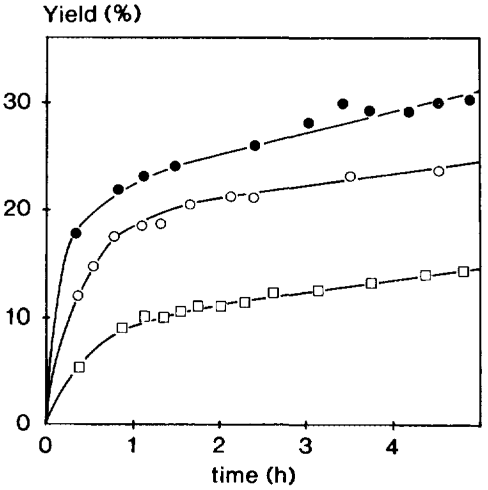


FIG. 6. Yield in nitrobenzene during the oxidation of aniline over various V-substituted molecular sieves: (●) VAPO-5 (sample 11), (○) V-HMS (sample 15), and (□) V-HMS (sample 10). Reaction conditions: see legend of Fig. 5.

Previous results had shown that homogeneous catalysis of aniline with TBHP led to the very selective formation of NB over vanadium compounds (8), whereas AZY was the major product formed over titanium catalysts (7). To explain the formation of NB in the presence of $VO(acac)_2$, Howe and Hiatt (8) proposed a mechanism in which phenylhydroxylamine was formed and subsequently oxidized to NB. The possible formation of NSB was not suggested. Over Ti catalysts, PH is probably also formed from the oxidation of aniline with TBHP, but not directly oxidized to NB.

To explain the difference between Ti and V active centers, we have to consider the adsorption of the different molecules on the surface of the catalyst. The first step is the adsorption of aniline from the solution (An_{sol}) on the solid surface (An_{ads}),

$$An_{sol} \rightarrow An_{ads},$$

followed by the formation of phenylhydroxylamine,

$$An_{ads} \xrightarrow{\text{TBHP}} PH_{ads}.$$

These steps are supposed to occur on both types of catalysts. Afterward, two different mechanisms can be proposed, depending on the nature of the catalyst.

Over Ti-HMS,

$$PH_{ads} \xrightarrow{\text{TBHP}} PH_{sol} + NSB_{ads} \rightarrow PH_{sol} + NSB_{sol}$$

$$NSB_{ads} + PH_{sol} \rightarrow AZY_{ads}$$

$$NSB_{sol} + PH_{sol} \rightarrow AZY_{sol}.$$

TABLE 2

Product Selectivities for the Oxidation of Aniline with H_2O_2 or TBHP over Ti-HMS (Sample 8) with Various Oxidant/Aniline Ratios

	H_2O_2				TBHP			
Ox/An	NSB[a]	AZO	AZY	NB	NSB	AZO	AZY	NB
0.2	0	12.5	87.5	0	0	21	79	0
2	0	8	92	0	2.5	25	74	0
6	0	25	44	31	3.5	15.5	55	26

Note. Reaction conditions: 0.25 g catalyst, solvent = acetonitrile, reaction time = 5 h, $T = 70°C$.

[a] The selectivity is defined as 100 × NSB/(NSB + AZO + AZY + NB).

PH is probably much more strongly adsorbed on V active sites, which makes that reaction of different molecules in the solution relatively unlikely to occur.

$$PH_{ads} \xrightarrow{TBHP} NSB_{ads} \xrightarrow{TBHP} NB_{ads}$$

Finally,

$$NB_{ads} \rightarrow NB_{sol}.$$

Concerning V-HMS, the difference in activity when using H_2O_2 or TBHP as the oxidant might be attributed to rather different geometries of the metal–peroxo compounds (30). Moreover, H_2O_2 generally associates much more strongly than TBHP to V(V) species (the association constants are in a ratio of about 200:1). Therefore, very important differences in activity can be observed with H_2O_2 or TBHP, as is the case for the oxidation of sulphides (31) or substituted aromatics (29).

However, NB could also be obtained over Ti-HMS when high TBHP or H_2O_2 concentrations were used (Table 2).

In catalytic oxidations with PCWP, Sakaue *et al.* (2) had shown that the solvent could play a very important role. In particular, $CHCl_3$ gave very high yields whereas no reaction was observed in methanol. When the reaction was performed over TS-1, two groups of solvents could be distinguished (12). The first one, which contained chloroform, water, acetonitrile, and methanol, gave a rapid formation of AZY with a very high selectivity at the end of the reaction. In contrast, the conversion of aniline was rather low in acetone or *tert*-butyl alcohol. This behaviour had been attributed to a size effect; these solvents were too large to enter the TS-1 channels. Nevertheless, we did not find any solvent in which no reaction occurred.

With TBHP, VAPO-5 is only active when reactions are performed in chlorobenzene. NB is not detected, even at the level of traces in ^tBuOH or acetonitrile. In contrast, the rate of formation of NB is higher in MeCN than in chlorobenzene when V-HMS is used as catalyst. The same trend is observed for the formation of AZY over Ti-HMS (Table 3). Therefore, the role of the solvent seems to be more critical with TBHP than with H_2O_2.

III. Effect of the Oxidant/Aniline Ratio

Oxidation reactions in the liquid phase are usually performed with low oxidant/substrate ratios. One of the major reasons is that using high oxidant/substrate ratios leads to the formation of overoxidized products, and that tends to decrease the selectivity. However, it was reported that it was necessary to use H_2O_2/Aniline ratios >3 to obtain the selective formation of NSB with homogeneous processes (9).

Our previous results over TS-1 (12) had shown that the product distribution was not really affected when H_2O_2/aniline increased from 0.2 to 0.8. Only small amounts of NB were detected when the ratio was equal to 1.6.

A very interesting observation was that the initial rate of formation of AZY was not dependent on the initial concentration in hydrogen peroxide. This was characteristic of diffusion limitations, attributed to the small pore opening of the zeolite.

We have performed similar experiments with H_2O_2 and TBHP over Ti-substituted mesoporous molecular sieves. As the rate of formation of AZY was very high under standard conditions with H_2O_2, reactions were carried out with 0.05 g of catalyst. The conversion of aniline was then sufficiently low to clearly estimate the modifications due to changes in H_2O_2/aniline ratios.

Figure 7 shows the formation of AZY over Ti-HMS (sample 8) for H_2O_2/aniline = 0.2 and 0.4. Even though the amount of catalyst is 10 times lower than in the case of TS-1, the catalyst is still very active. It is clear that the rate of formation of AZY increases with the initial

TABLE 3

Effect of the Nature of the Solvent on the Rate Constant for the Oxidation of Aniline with TBHP on Various Catalysts

	k (mmol/h g)	
Catalyst	Acetonitrile	Chlorobenzene
8	6.3	0.4
10	6.5	1.5
11	0.65	32

Note. Reaction conditions: 0.25 g catalyst, $T = 70°C$, TBHP/aniline = 2.

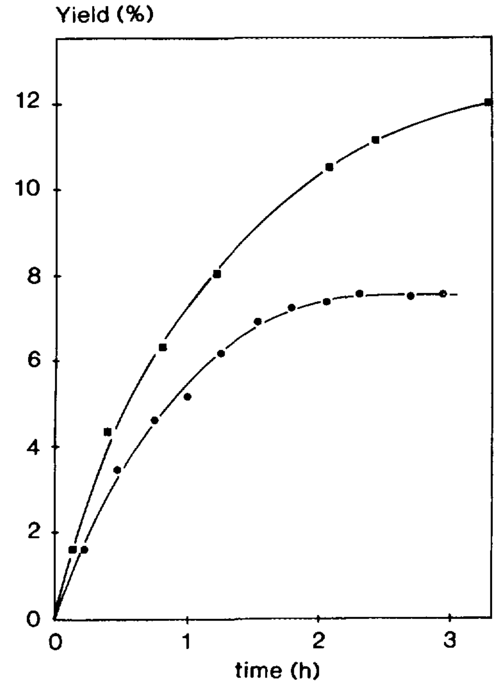


FIG. 7. Yield in azoxybenzene during the oxidation of aniline with H_2O_2 over Ti-HMS (sample 8): H_2O_2/aniline = 0.2 (●) and 0.4 (■). Reaction conditions: 0.05 g catalyst, T = 70°C, solvent = acetonitrile.

concentration in hydrogen peroxide. This behaviour is different from what had been observed over TS-1 and confirms that the reaction was limited by diffusion over medium pore zeolites.

Very similar results are obtained using TBHP as the oxidant (Fig. 8). The initial rate of the reaction increases from TBHP/aniline = 0.2 to TBHP/aniline = 2. In all cases, AZY is the major product formed, but AZO and NSB are also detected.

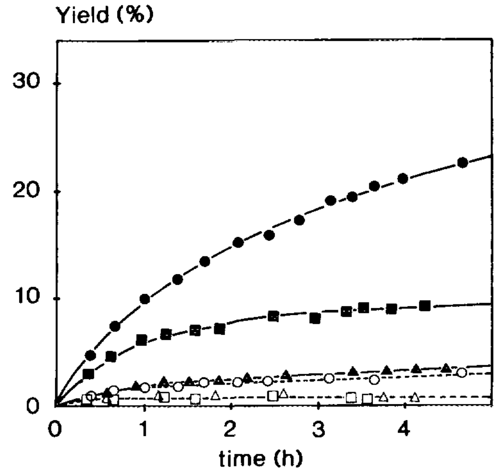


FIG. 8. Yield in azoxybenzene (filled symbols) and azobenzene (open symbols) during the oxidation of aniline with different amounts of TBHP over Ti-HMS (sample 8): TBHP/aniline = 0.2 (▲, △); 0.6 (■, □); and 2 (●, ○).

TABLE 4

Rate Constants of Formation of Azoxybenzene over Ti-HMS Catalysts of Different Ti Contents Using H_2O_2 and TBHP as Oxidants

		k (mmol/h g)	
Catalyst	Si/Ti	H_2O_2 as oxidant	TBHP as oxidant
8	85	267	6.3
12	54	690	10.2
13	31	—	18.5

Note. Reaction conditions: with H_2O_2, H_2O_2/aniline = 0.2, 0.05 g catalyst, solvent = acetonitrile; with TBHP, TBHP/aniline = 2, 0.25 g catalyst, solvent = acetonitrile.

It is interesting to note that the amount of AZO formed does not strongly depend on the TBHP concentration but the AZO selectivity is lower than when the reaction is performed with 0.25 g of Ti-HMS.

IV. Influence of the Metal Content

Two different routes can be followed to change the number of metal active sites in the catalytic reaction. The first consists of increasing the amount of catalyst and the second of using solids with various Si/Me contents. Comparison of the experimental data obtained by the two methods generally gives information about possible limitations due to diffusional processes in the zeolite pores.

Previous experiments performed over a series of TS-1 samples had shown that the rate of formation of AZY was not dependent on the Si/Ti ratio of the catalyst (12). In contrast, it was almost proportional to the amount of TS-1 used, thus confirming that the reaction was limited by diffusion of reagents and/or products in the channels of the molecular sieve. Similar experiments performed over Ti-HMS with hydrogen peroxide show that the rate of formation of AZY increases with the titanium content in the material (Table 4). This is in line with the total absence of diffusion limitations. Of course, as in the case of TS-1, the rate of formation of AZY also increases with the amount of catalyst.

In fact, because of the very large dimensions of the mesopores (28 Å) as compared to molecular sizes (6–7 Å), all Ti sites can be considered as "surface sites" immediately accessible to peroxide molecules.

Similar conclusions can be drawn from experiments carried out with TBHP over either Ti-HMS (Table 4) or V-HMS (Fig. 6).

CONCLUSION

We have shown that many transition metal substituted molecular sieves could be used as catalysts in the liquid phase oxidation of aniline with aqueous H_2O_2 and alkylperoxides. Even though TS-1 has a very good activity in this reaction, it is probably not the best catalyst; the reaction is limited by diffusion of products and/or reactants in the pores of the zeolite. This is also true for other medium pore zeolites such as ZSM-48. Large pore zeolites or mesoporous silica are preferred as they permit the use of bulky oxidants such as TBHP. The main products formed over Ti-containing catalysts are NSB, AZO, and AZY. For low H_2O_2/aniline ratios, selectivities up to 95% in AZY can be obtained for 100% conversion in hydrogen peroxide. Increasing the H_2O_2/aniline ratio leads to the formation of nitrobenzene.

The use of TBHP as oxidant considerably increases the selectivity in AZO. We suggested that this molecule could be formed via a noncatalytic route involving radicals. Surprisingly, NB is only detected for high TBHP/aniline ratios (>6), contrasting with results of homogeneous processes.

Vanadium-substituted molecular sieves, and particularly V-HMS, are only active when TBHP is used as oxidant; aniline is then converted very selectively into NB. The difference between Ti- and V-HMS is attributed either to more oxidant species in V-HMS or to different mechanisms of reaction.

For all catalysts, the reaction is largely dependent on the nature of the solvent. Reactions performed with TBHP over V-HMS give high yields in acetonitrile and only traces of NB and NSB in chlorobenzene. On the other hand, VAPO-5 is not active in MeCN but only in chlorobenzene.

Substituted mesoporous silicas seem to be very promising catalysts for the oxidation of submitted arylamines in the liquid phase. Indeed, Sonawane *et al.* (3) have reported that the performances of TS-1 were considerably diminished for methylaniline with respect to aniline and that the catalyst was even no more active in the oxidation of cyclohexylamine. The reason was most likely due to the small pore opening of the MFI structure. The use of Ti-HMS would probably greatly increase the amine conversion with very high selectivities in oxygenated compounds.

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