

A highly efficient oxidation of cyclohexane over Au/ZSM-5 molecular sieve catalyst with oxygen as oxidant

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A highly efficient oxidation of cyclohexane to cyclohexanol and cyclohexanone is accomplished over calcined Au/ZSM-5 molecular sieve catalyst with oxygen as oxidant.

The oxidation of cyclohexane to cyclohexanol and cyclohexanone is a key process in the chemical industry, for the oxidation products of cyclohexane, *via* cyclohexanol and cyclohexanone, are important intermediates in the production of caprolactam and adipic acid which are used in the manufacture of nylon-6 and nylon-66 polymers.^{1–4} The present commercial process for cyclohexane oxidation is carried out at around 150 °C and 1–2 MPa pressure with ~ 4% conversion and 70–85% selectivity to cyclohexane and cyclohexanol.⁵ The greater demand for these oxidation products and the high-energy intensity of the present process warrant a replacement with a more effective catalytic process. The increased environmental concerns in recent years call for benign oxidations such as molecular oxygen or hydrogen peroxide.^{6,7} VPO has been the most stable and active catalyst reported so far where hydrogen peroxide was used as the oxidant.⁸ A calcined VPO catalyst with a P/V ratio of 1.1 was found to give 91% conversion and a turnover of 400, with the following product distribution: 36% cyclohexanol, 64% cyclohexanone. In processes using oxygen as oxidant, they resulted in a more selective process with three important advantages:⁷ the facility to separate the catalyst after the reaction, lower energy costs and a higher stability regarding the irreversible reaction of over-oxidation products. To the best of our knowledge, Thomas *et al.*⁹ prepared isolated four-coordinate metal ions (Mn(III), Fe(III) and Co(III)) containing aluminophosphate molecular sieves. These catalysts were used in the cyclohexane oxidation with air as oxidation. Mn-AlPO-36 was the most active system, giving after 24 h at 403 K and 1.5 MPa air pressure, 13% conversion and a turnover of 233, with the following product distribution: 15% cyclohexanol, 47% cyclohexanone and 33% adipic acid. In the last decade, many heterogeneous catalysts which include oxides, metal cations and complexes incorporated on inorganic matrixes such as silica, alumina, zirconia, active carbon and zeolites have been developed for this reaction.⁶ Other notable catalysts include titanium containing mesoporous materials such as TS-1, Ti-MCM-41 and metal containing AlPO redox molecular sieves; however most of them give low conversions and turnover numbers.^{10–12} Especially because of environmental concerns, a greater demand for replacing reaction solvents with a more benign solvent or even without any solvent has become more attractive in recent years. But for the oxidation of cyclohexane, the solvent, which determines the polarity of the medium in the reaction system, plays an important role in the activity of catalysts.^{13,14} From this viewpoint, solvent free systems also urgently need to be developed.

Gold-based catalysts that were regarded as poor catalysts in past years have received particular attention in connection with the environmental protection. Nano gold catalysts supported on various metal hydroxides, oxides or zeolites have been utilized in a series of reactions.^{15–17} However, this has not been sufficiently explored for the cyclohexane oxidation. Herein we report a highly efficient oxidation of cyclohexane over calcined Au/ZSM-5 catalyst in an environmentally benign oxidation protocol involving oxygen as oxidant in a solvent free system.

Au/ZSM-5 samples were hydrothermally synthesized according to a classical ZSM-5 synthesis procedure. In a typical synthesis of ZSM-5 supported Au catalyst, the gel composition was 3.2Na₂O·x-Au·60SiO₂·960H₂O. 0.01 mol HAuCl₄·4H₂O was previously dissolved in a mixture of 8.3 g tetrapropylammonium bromide and 87 g water at moderate temperature (Solution A). Separately 41.8 g sodium silicate (*ca.* 27% SiO₂) was dissolved in 22 g water (Solution B) and 63.2 g NaCl in 25 g water (Solution C). Solution A and B were then added in portions in to Solution C under stirring, and the mixture was stirred for another 2 h. After aging at 170–180 °C for 72 h in a Teflon-lined autoclave, then the crystals were separated from the mother liquor, washed with doubly distilled water, dried and calcined at 550 °C for 5 h in air. Following this procedure, Au/ZSM-5 catalysts containing 1.30, 1.25, 0.55, 0.51 wt% Au were produced, labeled A, B, C and D, respectively. All of samples were characterized by XRD, ICP, UV–vis, XPS and N₂ adsorption/desorption. In a typical reaction procedure, cyclohexane (18.5 mmol) was mixed with calcined Au-ZSM-5 catalyst (5 mg) and heated to 150 °C under vigorous stirring in a 1 MPa O₂ atmosphere. After reaction, the reactants and products were directly analyzed by GC-MS and GC.

The chemical composition of the samples, the BET surface area and the pore volume are shown in Table 1. The BET surface area of the ZSM-5 is 415 m²g⁻¹. The loading of gold had only a modest effect on the surface area of the support. Taking the ZSM-5 sample as a reference, we evaluated the crystallinity of the Au-containing zeolite from the intensity of the typical peaks 501, 051, 151, 303, and 133, following the usual procedure. The results show a slight decrease in crystallinity due to the presence of Au. No expansion of the cell volume was observed for the Au/ZSM-5 samples compared to the ZSM-5 sample, suggesting that Au, as expected due to its big cluster volume, did not isomorphously substitute the Si⁴⁺ in framework position. Au is found inside the channel system or deposited on the external surface of the crystal. In the UV–vis spectra (Fig. 1) of ZSM-5 and Au/ZSM-5(A, B, C, D), the typical plasmon band of small Au particles between 500 and 600 nm is evident.^{18,19} For the ZSM-5 supported gold catalysts prepared by sol–gel and hydrothermal methods, the spectra in Fig. 1 reveal the expected trend that the bandwidth decreases with increasing Au loading. The XPS spectra of the 4f region show Au 4f_{5/2} and Au 4f_{7/2} peaks centered at about 88.45 eV and 84.79 eV, which were similar to the binding energy of bulk gold, indicating that most of the gold particles are present in the metallic state over the ZSM-5 surface.

The results of cyclohexane oxidation over calcined Au/ZSM-5 catalysts in the presence of an oxygen atmosphere have been

Table 1 ICP-AES data and BET surface area of various Au/ZSM-5

Catalyst	Au content (%)	BET surface area/m ² g ⁻¹	Pore volume/cm ³ g ⁻¹
ZSM-5	0	415	0.110
Au/ZSM-5(A)	1.30	421	0.122
Au/ZSM-5(B)	1.25	433	0.118
Au/ZSM-5(C)	0.55	420	0.115
Au/ZSM-5(D)	0.51	414	0.131

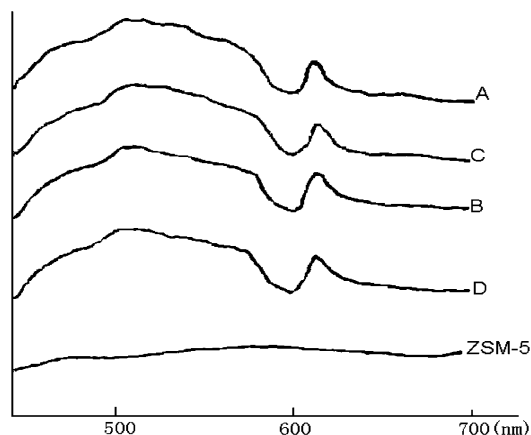


Fig. 1 UV-vis patterns of various supported Au ZSM-5 with different Au loadings (A. 1.30 wt%; B. 1.25 wt%; C. 0.55 wt%; D. 0.51 wt%)

compared with that under a nitrogen atmosphere (Table 2). A highly efficient and quantitative oxidation of cyclohexane to cyclohexanol and cyclohexanone could be accomplished at 150 °C under 1 MPa O₂ atmosphere over Au/ZSM-5 catalysts with different Au contents. Compared with other catalysts (entry 11, 12), even without any free-radical scavenger, the results we report are excellent not only in conversion but also in selectivity. The reaction time in our catalytic system was greatly shortened. TON as high as 3096, which is better than any of the catalyst systems reported earlier, could be achieved. The result listed in entry 10 shows that the unregenerated Au/ZSM-5 essentially retained its catalytic activity during the period of its reuse. A slight decrease in the conversion of cyclohexane could be due to loss of some catalyst during filtration and no addition of any fresh catalyst to keep the amount of catalyst used the same. Fig. 2 shows the influence of reaction temperature, and it is clear from the figure that the yield of both products appears to decrease with temperature. At higher

Table 2 Cyclohexane oxidation over Au/ZSM-5 catalyst^a

Entry	T/°C	Cat. Au/ ZSM-5	t/h	Con.(%)	Selectivity (%)		TON/ h ⁻¹
					Cyclo- hexanol	Cyclo- hexanone	
1 ^b	150	A	5	No reaction			
2	150	A	1	No reaction			
3	150	A	2	6	44	52	1681
4	150	A	3	15	24	68	2802
5	150	A	4	16	25	67	2242
6	150	A	5	11	26	70	1233
7	150	B	3	9	31	66	1508
8	150	C	3	7	36	55	3092
9	150	D	3	6.5	27	73	3096
10 ^c	150	A	3	14	26	66	2617
11 ^{de}	130	MnAlPO-5	24	6	19	43	107
12 ^f	130	MnAlPO-5	24	16.5	20	43	292

^a Cyclohexane (18.5 mmol); the amount of catalyst in entries 1–10 was 5 mg; 150 °C, 1 MPa O₂ or N₂, stirrer. ^b Entry 1 was carried out under 1 MPa nitrogen; entries 2–9 were carried out under 1 MPa oxygen. ^c The catalyst Au-ZSM-5 with a Si/Au ratio of 100 was recycled 3 times. ^d Moles of substrate converted per mole of metal (Au, Mn) in the catalyst. ^e The results (entries 11, 12) were obtained from reference 12. ^f Reaction carried out in the presence of air and small amounts (3 wt% wrt cyclohexane) of hydroquinone (free-radical scavenger) (from reference 12).

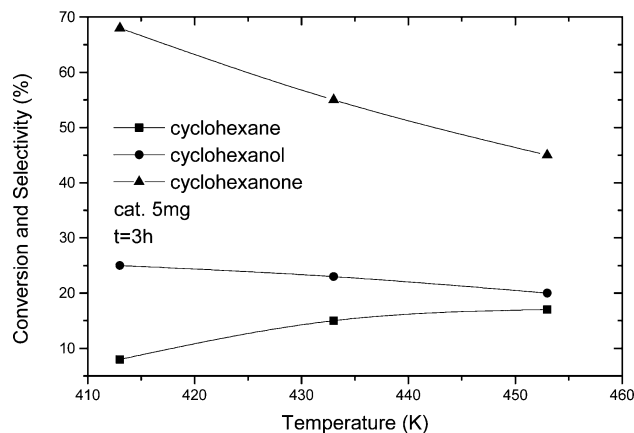


Fig. 2 Effect of reaction temperature on the conversion and selectivity over Au/ZSM-5 (A).

reaction temperature (453 K), the total selectivity of cyclohexanol and cyclohexanone decreases.

In summary, a calcined Au/ZSM-5 catalyst is found to be a very efficient catalyst for the quantitative oxidation of cyclohexane using oxygen as oxidant in a solvent free system, and the catalyst can be recycled twice without any obviously loss of activity.

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